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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

A Look at Techniques for the Dimensional Calibration of Standard Microscopic Particles

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Standard Reference Materials:

A Look at Techniques for the Dimensional Calibration of Standard Microscopic Particles

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PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are well-characterized materials produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system are carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

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CONTENTS

	Page
Executive Summary	x
1. INTRODUCTION	2
A. Sample of Users' Needs	2
B. Current Techniques	3
1.B.1. Available Instrumentation: Reviews	3
1.B.2. Documentary Standards	3
1.B.3. Standard Reference Particles	3
2. SUMMARY OVERVIEW OF ELEMENTS OF PARTICLE SIZE MEASUREMENT SYSTEMS	8
A. The Object: States of Matter	8
B. The Measuring Instruments	8
2.B.1. Size-Dependent Phenomena	8
2.B.2. Number of Particles Involved	12
2.B.3. Separation of Particles by Size	12
2.B.4. Types of Dimensional Calibration	12
C. Single Number Index to Characterize Particle Dimensions	18
2.C.1. Characterizing a Single Particle	18
2.C.2. Giving an Average Size to a Group	20
3. CANDIDATE INSTRUMENTS FOR STANDARDS CALIBRATION	25
A. Needs of Calibration Scheme	25
B. Interrelationship of Three Candidate Measurement Methods	25
3.B.1. Electron Microscopy	25
3.B.2. Light-Scattering	28
3.B.3. Automatic Counting (and Sizing) of Particles	33
4. INTERCOMPARISON OF MEASUREMENTS	38
A. Comparison of Latex Particle Measurements	38
4.A.1. Specific Results Compared	38
4.A.2. Generalization from Comparisons	70
5. REPORT CONCLUSION	85
6. BIBLIOGRAPHY	86
7. APPENDICES	99
A. Identified Domestic Suppliers of Standard Spherical Particles or Test Dusts	99
B. Some International Suppliers of Particle-Size Related Equipment	100
C. Documentary Standards Related to Microscopic Particle Size Measurement	106
D. Literature Sources Consulted	110
E. University and Industry People Contacted	112
F. NBS Certificate of Calibration for Glass Spheres SRM 1003, 1004, 1017a, 1018a; Scanning Electron Microscope Magnification Standard (A Stage Micrometer Scale), SRM 484a	114
G. Tolerances Attached to the Average Quoted in Certain Tables	135

Executive Summary

The purpose of this report is to examine the metrological capabilities of various generic techniques suitable for use at NBS for the dimensional calibration of future NBS particle size Standard Reference Materials (SRMs). At present, within the overall range of sizes from 100 μm to 0.1 μm , some sized glass beads, spherical polymers, pollens, and test dusts are commercially available as reference materials. Currently, NBS provides as SRMs only some wide-size-distribution glass beads. The intent is to develop other particle-size SRMs: initially, narrow-distribution spherical polymers and, finally, stable particulate matter of arbitrary shape and size distributions.

At the present level of development of calibration technology, the spherical polymers are most suitable for an initial SRM. They are highly spherical, and have narrow size distributions, thus providing for minimal ambiguity in measurements and maximal separation of object and instrument variables. Batch-manufactured spherical polymers range in size from less than 80 nm to over 100 μm with size distributions characterized by standard deviations which range in a complex manner from about 5 nm for the smallest particles to 1-10 μm for the largest.

The report explicitly looks at various size-dependent phenomena which are the basis for measurement techniques. It examines the way an individual particle is given one characteristic dimension, and how a collection of particles is given an average dimension. Of the variety of techniques examined, three generic ones have been singled out from those with individual characteristics which contribute to a comprehensive calibration approach.

Microscopy which gives direct-imaging includes both optical which is limited by depth of focus and electron which has high resolution and great depth of focus. Electron microscopy can provide direct-imaging, shape-verifying definitive measurements of limited numbers of particles in vacuo. For polystyrene, a glassy polymer, there is evidence that the required evacuation and electron-irradiation can be used without producing significant dimensional changes. Transmission electron microscope measurements on polymer spheres by the manufacturer over nearly three decades show consistency at 5 to 10 nm level with some indication of a systematic difference of 15 nm from an average of light-scatter and other electron microscopy values.

Light-scattering techniques vary considerably in detail but generally are one of two fundamentally different types: the first determines size from the intensity characteristics of scattered light with analysis based on Mie calculations for scattering of a plane wave from a uniform dielectric sphere; the second determines size from the frequency characteristics of scattered light with analysis based on hydrodynamic calculations for objects moving in fluids. The former, angular-intensity type, is of specific interest as a means to obtain first-principle measurements potentially accurate at the 1% level on highly-spherical, narrow-distribution particles. The calculations assume particles are spheres with a known index of refraction. Briefly noted in the report are other light-scattering techniques with demonstrated capability for calibration quality particle size measurements such as Rayleigh spectrometry, laser Doppler, and single-particle levitation; from among the suitable techniques, the angular-intensity one has been chosen for initial calibrations and for description here for reasons of directness in implementation, use, and interpretation.

Automatic liquid-borne particle counters measure some characteristic dimension of individual particles passing sequentially past a detector. There are two fundamentally different types: (1) the electrical-resistivity type measures the volume of electrolyte displaced by a particle; and (2) the optical type which can be of two kinds: (a) one measures a projected shadow area; and (b) the other measures a Fraunhofer-diffraction pattern dimension. The optical types measure dimensions down to about 2 μm while the electrical-resistivity types measure down to about 0.5 μm . All three devices can give explicit histograms of size distributions but are comparators which require particles of known size for calibration. Reproducibility of comparisons of mean diameters are of the order of 1% to 3%.

Within the body and seven appendices, this report contains 50 tables of data, 250

literature references, and lists of 10 domestic commercial suppliers of sized particles, 30 principal and 40 secondary documentary standards on particles, 22 industry and university contacts, and 125 domestic and foreign suppliers of particle-sizing equipment.

The report concludes that the definitive calibration of narrow-distribution polymer spheres, a prerequisite first step toward size-calibration of irregularly-shaped matter, can be obtained by a three-element, self-consistent approach involving the three techniques named: electron microscopy to provide direct-view shape-verification and direct measurement of a limited sample of particles in vacuo; liquid-borne counting to provide an explicit histogram verification of the broad size distribution in a sample liquid; and angular-intensity light scattering to provide a nondestructive mean-size measurement of the original population in the delivery vial. Under these conditions, an overall uncertainty in calibration of 0.005 μm or 1%, whichever is greater, is anticipated as achievable.

List of Tables

<u>Table No.</u>	<u>Page No.</u>
1. Examples of Commercial Sized Standard Particles	6
2. NBS Standard Reference Materials Related to Particle Sizing	7
3. Some Definitions of Particle Size	19
4. Shape Factors and Shape Coefficients.	21
5. Expressions for Various Mean Diameters.	22
6. Various Techniques: Dow Nominal 2.956 μm Latex	39
7. Various Techniques: Dow Nominal 2.682 μm Latex	40
8. Various Techniques: Dow Nominal 1.192 μm Latex	41
9. Various Techniques: Dow Nominal 0.796 μm Latex	42
10. Various Techniques: Dow Nominal 0.264 μm Latex	43
11. Various Techniques: Dow Nominal 0.088 μm Latex	44
12. Various Techniques: Eleven Other Dow Latexes	46
13. Resistance Counter I-vs-EM: Six Standard Latexes	47
14. Resistance Counter III-vs-EM: Two PVC Latexes.	48
15. Resistance Counter II-vs-EM: Six Standard Latexes.	49
16. Resistance Counter I-vs-II: Four Standard Latexes.	50
17. Resistance Counter Round-Robin: Three Devices, One Latex	51
18. Resistance Counter-vs-Optical Microscope: Four DVB	52
19. Visual Eyepiece, Array, SEM: Four DVB Latexes.	53
20. Filar-Eyepiece Microscope-vs-EM: Seven Dow Latexes	54
21. Optical Array-vs-EM: Six PVC Latexes	55
22. EM of Shadow-vs-Particle Images: Five PVC Latexes.	56
23. EM of Shadow-vs-Particle Images: Four DVB Latexes.	57
24. Dark-Field Optical Microscope-vs-EM: Four PS Latexes	59
25. Disc Centrifuge-vs-EM: Six PVC Latexes	60
26. Fractional Creaming-vs-EM: Four PVC Latexes.	61
27. Flow Microscopy-vs-EM: Nine Dow Latexes.	62
28. HOTS-vs-EM: Six PVC Latexes.	63
29. HOTS-vs-EM: Six Dow Latexes.	64
30. Light Scattering by Five Techniques and Same Workers: Eight Dow Latexes.	65
31. Rayleigh Linewidth-vs-EM: Four Dow Latexes	66

32. Average of Light Scattering: 0.245 μm Dow Latex.	67
33. Average of Light Scattering: 1.192 μm Dow Latex.	68
34. Average of Light Scattering: 2.956 μm Dow Latex.	69
35. Electron Microscopy (EM) of Dow-vs-Others: Twenty-One Latexes.	71
36. EM of Dow-vs-Davidson, et al.: Nine Dow Latexes.	72
37. Size Distributions of Nine Dow Latexes by Two EM Groups	73
38. Mean size of Nine Dow Latexes by Two EM Groups.	74
39. EM of Dow-vs-Dobbins, et al.: Six Dow Latexes.	75
40. EM of Dow-vs-Davidson, Haller: Four Dow Latexes.	76
41. EM Plate Image Size Measurement: Effect.	77
42. EM Plate Image Size Measurement: Five Latexes.	78
43. EM Dow-vs-EM Average of Others: Twenty-One Latexes	79
44. EM Dow-vs-LS Average: Fourteen Latexes	80
45. EM Other-vs-LS Average: Nine Latexes	81
46. Shadow EM-vs-Average EM and LS: Six Dow Latexes.	83
47. EM Dow-vs-Combined LS-EM: Twenty-Four Latexes.	84

List of Figures

<u>Figure No.</u>		<u>Page No.</u>
1.	The Width of the Particle Size Distribution (σ) as a Function of Mean Particle Diameter of the Distribution for Batch Grown Polymer Spheres Produced by One Manufacturer	5
2.	Alternative Ways of Measuring the Size of an Image	36

A LOOK AT TECHNIQUES FOR THE DIMENSIONAL CALIBRATION
OF STANDARD MICROSCOPIC PARTICLES

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This report surveys generic techniques for the dimensional calibration of microscopic particle size standards. It notes some user needs and available instrumentation, documentary standards, and commercial, sized particles. It discusses the elements of the measurement process, including the particle and medium, size-dependent phenomena, shape factors, single-number indices of average size, and means of length calibration. The report examines systematic differences among published results of electron microscopy, light scattering, particle counter, and other measurements on widely-used commercial polymer spheres. It concludes that the definitive calibration of narrow-distribution polymer spheres, a prerequisite first step toward calibration of irregularly-shaped matter, would best involve a three-element approach involving the techniques named.

Key Words: Dimensional measurement; electron microscopy, flow-through particle counters; latex spheres; light scatter; micrometrology; microscopic spheres; Mie scattering; particle standards; optical microscopy; particle size calibration; polymer spheres; scanning electron microscope; transmission electron microscope.

1. INTRODUCTION

Particle-size measurement is an inclusive term that encompasses a diversity of measurements by a spectrum of techniques on a host of different particulate substances. To calibrate particle-size measuring devices, particles of "certified size" are available from commercial sources. At the same time, requests for NBS-certified, particle-size Standard Reference Materials (SRMs) have been insistent and recurrent (for example, Refs. C1, K5, W10).

As part of an investigative-developmental project at NBS on such SRMs, this report has been prepared. Its purpose is to look at those techniques which can potentially be used as (1) reference methods for the definitive, primary dimensional-calibration of particle standards and (2) comparison methods for convenient transfer calibration from the reference method to bulk calibration method.

Guided by experience at NBS and the preponderance of work of a more fundamental nature reported in the scientific literature, this report has of necessity focussed on the basic techniques of electron microscopy and light scattering and the comparison techniques of automatic particle counting. An underlying premise of the report is that in order to understand and manage the basic measurement techniques, the object-to-be-measured should be as simple and lacking ambiguity as possible. Hence, because of their unique metrological properties, latex spheres play a central role in the examination of individual techniques and their intercomparisons.

In its structure, this report follows the topical outline given in the Table of Contents. Part I is introductory background on particles and their size-measurement as generally practiced. Part II outlines some of the basic metrological factors of measurement systems to be taken into explicit account. In Part III, candidate instruments are looked at individually, and in Part IV their measurement results are intercompared. Part V summarizes the general conclusions of the report, and Part VI lists references. Part VII includes appendices on domestic suppliers of particle reference materials, equipment suppliers, documentary standards, bibliographic sources used, and contacts at universities and in industry. Also included is a note on how some quoted statistical uncertainties are computed.

A. Sample of Users' Needs

A vast spectrum of end-products, by-products, and waste-products or contaminants of modern industrial technology are microscopic particles which require dimensional measurement. As end-products, particles can be constituents of anything from plastics to cement to metal ores to photographic emulsions. As end products or by-products particles can be the result of manufacturing processes as varied as milling, mining, refining, grinding, spraying, or chemical precipitation. As contaminants, particles can occur in drugs and intravenous fluids for medical use, in lithographic chemicals for microelectronics manufacture, in hydraulic fluids for aerospace systems, and in the atmospheres industrial workers and the general population breathe.

Particles which require dimensional measurement vary greatly in range of size, chemical composition, and uniformity of size and shape. What various workers refer to as particles range in characteristic dimension over as many as six orders of magnitude: from 10,000 to 0.01 micrometers (μm) [A14]. They vary in physical make-up from complex-but-stable, naturally-occurring minerals (asbestos) or biological material (cotton dust), to mixed and dynamically changing smoke and combustion products, to pure and stable synthesized materials such as polymers. Individual particles vary in shape from jagged irregular road dusts, to fibrous (actually rolled-plates) asbestos, to disc-like blood platelets, to spheroidal bacteria or pollens, to spherical polymer resins. Populations of particles range from

Materials and instruments are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or instrumentation is the best available for the purpose.

heterogeneous mixtures of irregularly shaped debris of widely different average size to collections of nearly perfect spheres of nearly identical sizes.

B. Current Techniques

1.B.1. Available Instrumentation: Reviews

The instrumentation developed to dimensionally measure these diverse particles - apart from the equipment to collect and separate them - is as varied as the particles themselves. The instruments vary in fundamental principle of operation, the size-dependent attribute of the particle measured, range of sizes measurable, resolution, precision and accuracy. Physical phenomena used as bases for dimensional measurements include: direct imaging by light and electron optics; light scattering of a multitude of types; X ray, Y ray, ultrasonic and acoustic attenuation; pressure, flow, magnetic, electrostatic, or resistivity variations; and settling, sieving, separation, diffusion, and other properties.

Over the last few years, reviews of particle-size measurement instrumentation have been published in archival journals, trade magazines, monographs, and engineering text books. For example:

A comprehensive survey of instrumentation was reported by Davies in 1974-75 [D11, D12, D13]. It was further updated and revised in 1978 [D8]. A popularized view of some commercial instruments and related techniques was given by Austin [A14] and Carver [C1]. Stockham and Fochtman [S10] discussed, among other aspects of particle size analysis, a range of instruments and techniques [S10]. Collins, et al., [C21] reviewed the common methods of measurement while other reviewers such as Kratochvil [K13] considered a general technique, such as light scattering, as it applied to particle-size measurement. Others, who will be referenced later in this report, compared specific techniques with each other. Finally, Allen [A3], in his textbook on particle-size measurement, provided a detailed and referenced discussion of phenomena, instruments, and techniques. Taken with the articles of Davies, Allen's compilation of commercial suppliers of instruments [Appendix B] provides a comprehensive list of available equipment and their sources.

1.B.2. Documentary Standards

Faced with a broad array of instruments and techniques which (after measuring different dimensional attributes of collections of irregularly shaped and compositionally varied particles) yield numbers called "particle size", industry takes the normal recourse and seeks suitable documentary and physical standards. Documentary standards are written descriptions of methods, procedures or specifications, for example, how to specify or test the performance of an instrument. Physical standards are artifacts, e.g., a particle of known size, by which one calibrates or tests an instrument or process.

The American National Standards Institute (ANSI) and the American Society for Testing and Materials (ASTM) as well as the National Fluid Power Association (NFPA) and the Society of Automotive Engineers (SAE) have documentary standards relating to particle size measurement. Appendix C lists seventeen ANSI, thirteen ASTM (existing or in draft), and three NFPA standards, as well as an SAE and an ISO (International Organization for Standardization) standard. It also gives the identification numbers of thirty-seven other ASTM standards, twenty-two of which are on material characterization and fifteen on system characterization.

1.B.3. Standard Reference Particles

Some of the documentary standards refer to physical reference materials; that is, sized, standard, and uniform particles or test dusts. Ten organizations have been identified as commercial domestic sources of sized particles [Appendix A]. These include: particle supply firms who make and/or handle standard reference particles as their primary business; manufacturers of particle-measuring instruments who make and/or supply reference particles for instrument calibration; and manufacturers of other products who produce sized-standard reference particles or dusts as a sideline.

There are four major types of commercially available, sized-standard reference particles suitable for calibration of particle-size measuring instruments. These include: test dusts; naturally occurring, spherical pollens; uniform glass beads or microspheres; and various polymer "latex" spheres. Examples of the characteristic dimensions of these various types of reference materials are given in Table 1. Commercial test dust is a collection of coarse, irregularly shaped particles primarily used to simulate the matter removed by filtration from hydraulic systems. Pollen, glass, and latex-type polymer particles are used as spherical particles to calibrate, for example, various flow-through particle counters, light scattering, and other particle-sizing instruments. Latex-type polymer spheres of small diameters are used as electron-microscope calibration standards.

Latex-like polymers and glass beads are most widely used as sized, spherical calibration reference materials, and each has physical properties which are advantageous in some applications, and drawbacks in others. The following sketches of their properties are drawn from a technical article by NBS workers on glass beads for calibrations [H18], glass bead and latex supplier's literature [Appendix C], and undocumented accounts by NBS workers and particle manufacturers.

Glass beads have the following properties: appear fairly spherical in direct observation; are transparent with a high index of refraction; are rigid solids without cleavage planes; are somewhat surface-tempered; and have impact strength. In addition, the glass beads can have voids and/or an onion-like layer structure, can shatter or fragment, can agglomerate in the presence of atmospheric moisture, have a broad distribution of sizes within a sample and mean sizes for the population typically which range from about 5 μm (or as low as 1 μm) to 100 μm .

Latex-like spheres (polystyrene, polyvinyl toluene, etc.) appear highly spherical, have low-or-moderate specific gravity, are translucent-to-opaque, are glassy-to plastic solids, and can distort in shape when dried or irradiated. Further, the latex-like spheres can have dimensions and properties dependent on surface-active and dispersal agents, cannot be airborne above about 3 μm in size, and can agglomerate in pairs, triads, or clumps. Mass-produced, batch-grown spheres can have a single, relatively narrow distribution of sizes while limited-production, droplet-grown spheres can have a very narrow "main-mode" size with "satellite modes," one below and one above the main-mode. Latexes cover the range 0.01 to 100 μm with distribution of size within populations strongly dependent on mean size. Batch-produced latex spheres have population standard deviations (σ) characterized as in Fig. 1 (drawn from a manufacturer's technical data sheets): below 1 μm mean size, is of the order of 0.005 μm ; it rises at 1 μm to about 0.01 μm and remains at 1% or so up to 2 μm , rising to 5% or 0.15 μm at 3 μm , 10% at 5 μm , and 20% at 10-20 μm . Droplet-produced latex spheres are reported by another manufacturer to have a "main-mode" distribution of less than 1.5% over the range of 5 to 100 μm . ("Satellite-modes" are not counted in the computation of this narrow width.)

At present, NBS provides, as standard reference materials, the sized glass beads and spheres described in Table 2, as well as a stage-micrometer also described. The basic method of calibration of the glass spheres and beads is described in Ref. H18 and in the certificates of calibration (example in Appendix G) which accompany the materials.

Also reported to be available from other sources are: encapsulated, graduated rows of individually selected particles [T4]; dyed latexes and ones to whose surface chemicals can be atomically bonded [B2, B3]; and specially sieved, narrow-distribution glass beads [C22]. Potentially available sometime after 1982 [E2] are narrow-distribution, large-diameter latex spheres batch grown in the gravity-free environment of the space shuttle [K8].

Among particle reference materials, latex-like polymer spheres play a central metrological role; and among the suppliers of latex-like spheres, the metrological role of the Dow-Diagnostic Division of Dow-Chemical Company* is unique. For over 25 years, latex spheres with individual particle diameters measured by electron microscopy and with mean diameters covering at close intervals the range from sub-0.1 μm to over 1 μm , have been distributed by Dow [B2, B3]. From 1954 until 1979, published values of latex diameters

*Please note disclaimer at beginning of Introduction.

have been measured at Dow by the same basic technique and often by the same individual [B16, R10]. Within the industrial and scientific communities, these latex particles have been measured by numerous other workers and techniques, and published accounts and results of these measurements provide a systematic and comprehensive body of metrological data and form a major portion of this report. Various aspects of the measurement techniques and instruments will be discussed in Parts II and III of the report while Part IV will present an examination of some of that data.

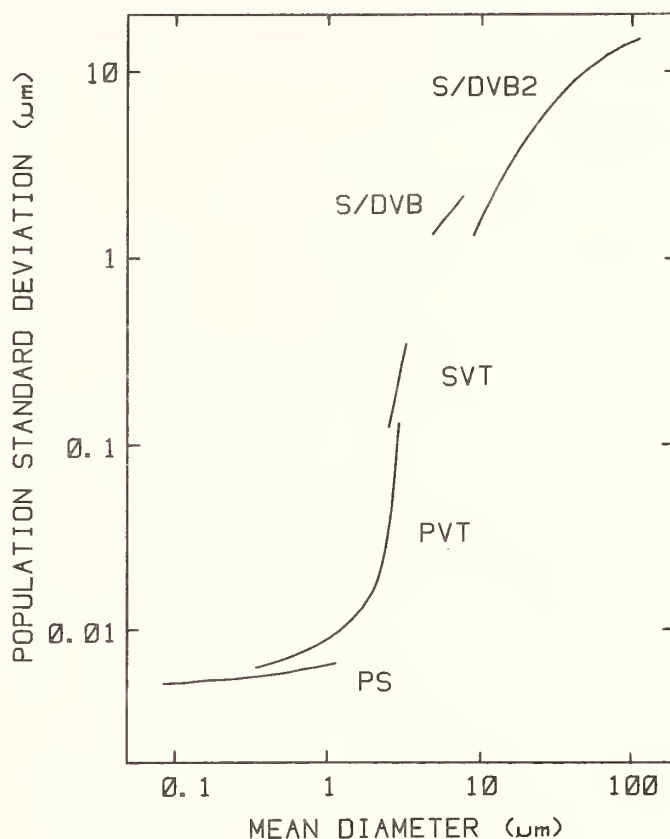


Figure 1. The width of the particle size distribution (σ) as a function of mean particle diameter of the distribution for batch grown polymer spheres produced by one manufacturer [Ref. B3].

Table 1

Examples of Commercially Available Sized Standard Particles

<u>Material</u>	<u>Mean Size (μm)</u>	<u>Range About Mean (μm)</u>
<u>Polymer Spheres</u>		
Polystyrene (PS)	(Great variety with size-dependent range; see figure 1 for typical values)*	
Polyvinyl-Toluene (PVT)		
Polystyrene-Divinyl Benzene (DVB)		
Polystyrene-Butadiene (PSB)		
<u>Uniform Glass Microspheres**</u>		
	-	1-3
	-	1-5
	7	1-30
	1.8	0.5-6
	8.0	4-14
	10	5-15
	.	
	100	90-115
	.	
<u>Spherical Pollens**</u>		
Paper Mulberry		13-14
Ragweed		19-21
Bermuda Grass		22-30
Walnut		40-50
Corn		65-75
<u>Test Dust**</u>		
AC Fine		1-45
AC Fine		45-80

*Suppliers Bulletin (Dow Diagnostics; see note below).

**Suppliers Bulletin (Duke Standards Inc.; for identified suppliers of standard particles see Appendix A.)

Table 2

NBS Standard Reference Materials Used in Particle Size Measurement		
Standard Reference Material Number	Type	Dimensions (μm)
SRM 1003	glass spheres	5-30
SRM 1004	glass beads	34-120
SRM 1017a	glass beads	100-310
SRM 1018a	glass beads	225-780
SRM 484a	SEM stage micrometer	1,2,3,5,50*

*Spacings calibrated to $\pm 0.04 \mu\text{m}$ in 1-5 μm range and 0.48 for 50 μm .

2. SUMMARY OVERVIEW OF ELEMENTS OF PARTICLE SIZE MEASUREMENT SYSTEMS

The purpose of particle-size measurement is to associate with the particles a number, that is, a "size," which characterizes some important dimensional property of the particles. The measurement process involves the particles as an object, the measuring instrument and a conceptual model of how it interacts with the object, and the mathematical manipulations done with the data collected on the particles.

This section will look at some of the combinations of object-instrument-mathematical models which give rise to different operational definitions of particle size. Specifically, the section briefly examines various kinds of particles and their environments, some measuring instruments and the size-dependent phenomena they exploit, conceptual definitions of particle size, and mathematical definitions of mean particle size.

A. The Object: State of Matter

Particles to be sized can be any one of the three states of matter as can the medium in which the particles exist. In aerosols, the medium is gaseous and the particles can be liquid drops or solids. In hydrosols, the medium is liquid and the particles are most often solids, although they may be drops of other liquids or air bubbles. When not suspended in a gaseous or liquid medium, solid particles can be in the form of a dry powder or dry individual particles. And finally, both liquid drops and solid particles can exist in an extremely low-pressure gaseous or vacuum medium.

As candidates for sized particle reference materials, solids have the attribute that they may be used in liquid, gaseous, or vacuum media with some degree of mechanical size and shape stability. For example, polymer spheres in water solution may be measured in that solution by (1) laser-light scattering, (2) in an electrolyte solution by a resistive-type, flow-through counter, (3) air-dried and on a substrate by an optical microscope, and (4) evacuated and irradiated in an electron microscope. By comparing sizes measured by different techniques, the effect on the size and shape of the particle by the change of medium can and should be considered explicitly.

B. The Measuring Instruments

At the heart of each operational definition of a particle size is a device which responds to some size-dependent property of the particles. The size-dependent phenomena may involve one or more particles at a time or may involve a physical separation of particles by size. Thus, some calibration by which the basic unit of length is associated with that phenomena is required. This section examines some of these phenomena, the number of particles involved, any separation process used, and the types of calibrations possible and useful.

2.B.1. Size-Dependent Phenomena

Initially, particle-size measuring instruments detect some signal which is assumed to be related to the size-property of the particle. For imaging-instruments, the intensity distribution in the directly viewable, magnified image of the microscopic particle is the signal. For non-imaging instruments, the nature of the signal depends on the phenomena exploited.

a. Imaging: Optical and Electron

Microscopes, both light-optical or electron-optical, are valuable for particle-size analysis because they present a direct-image of the particles to the investigator for visual examination. The visual image can contain information on shape, surface features, and debris present, as well as dimensional information. The reliability of the dimensional information obtained from microscopy depends, among other things, upon specifics of the instrument and technique. These specifics include the familiar matters of magnification, resolution limit, and depth of focus, and the less familiar matter of edge-location, with its dependence on a selection criterion and its variation with focus and other system variables.

In optical microscopy, the magnification in the image plane can be up to 1000 or 1500 X so that particles as small as $0.5\text{ }\mu\text{m}$ or so can be imaged. In reflected light, the surface features of the object and the shape of the plane section of the object perpendicular to the optical axis of the microscope are viewed, while in transmitted light, only the plane section can be seen.

In electron microscopy, the maximum magnification in the image plane depends on the type of microscope: for the scanning electron microscope (SEM), which forms images of the surface of solid objects, the magnification can be up to about 100,000 X while for the transmission electron microscope (TEM), which forms images from electrons which pass through thin specimens, the maximum magnification is typically 300,000 X but can reach 800,000 X. SEM's can image particles as small as $0.015\text{ }\mu\text{m}$, while the TEM's can image those as small as $0.001\text{ }\mu\text{m}$. As with the optical microscope with reflected light, the SEM images the surface and the plane section, while like the optical microscope with transmitted light, the TEM images the plane section only.

In addition to surpassing the optical microscope in maximum magnification by orders of magnitude, electron microscopes have the major advantage of sharper focus and greater depth of focus. Microscope images, whether optical or electron, do not have sharp, discontinuous edges, but are bounded by blurred transition regions. The width of the blur-region is a variable which depends on the instrument resolution and depth of focus capabilities as well as a subjective judgment of best focus.

In a dimensional measurement of an extended object, such as a particle or a planar feature, the apparent width depends on where in the blur region one decides the edge lies. The location of the edge therefore changes with the subjective criterion of edge location within the blur region and the location of the blur region varies with focus settings. There is clear evidence that filar-eyepieces, image-shearing (i.e. split image) eyepieces, and automatic-image analyzers, such as TV-microscope systems, locate the edges of optical images on different levels within the blur region [S11,12].

For an ideal object with square edges, the width of the blur region for an optical microscope is determined by the object and by diffraction phenomena modulated by the performance characteristics and focus setting of the microscope; for a real optical microscope and real object, the blur region will be greater than that for an ideal laminar object imaged by a diffraction-limited lens system. As a rule of thumb, the smallest blur attainable will be wider than about $0.25\text{ }\mu\text{m}$ [N5]. The location of each of two edges which define the width of an object's image (e.g., the diameter of a particle) is ambiguous by an amount twice as great or up to the full-diffraction spot, i.e., $0.5\text{ }\mu\text{m}$ or more, depending on edge-location criteria, focus choice, and instrument operating conditions.

It has been demonstrated that the apparent size of microscopic objects as measured by optical microscopy depends systematically on lens and diaphragm apertures [C8, N5, S3], illumination levels [C9], focus conditions [N5, S3] and image-measurement device type [S12]. It has been demonstrated experimentally that automatic-TV-microscope systems, filar-eyepiece visual microscopes, and image-shearing visual microscopes can yield size-measurements on identical 1 to $10\text{ }\mu\text{m}$ planar objects that differ systematically from -0.25 to $+0.25\text{ }\mu\text{m}$, depending on image polarity [S12]. Further, a related study [S11] showed systematic differences among measurement results from several industrial laboratories on a $3\text{ }\mu\text{m}$ planar object of up to $0.6\text{ }\mu\text{m}$. In these cases, the thickness of the object ($0.1\text{ }\mu\text{m}$) was advantageously small compared to the depth of focus of the optical microscope. In particle size measurement, this is not the case.

Classically, the depth of focus of an optical microscope is on the order of $0.5\text{ }\mu\text{m}$ at 1000 X (and, for example, $10\text{ }\mu\text{m}$ at 100 X). In such a situation, the depth of focus is a significant fraction of the large particles in a field of view (and can exceed the size of small ones in the same field). Attainment of an acceptable, albeit arbitrary, "best focus" is a major limitation on particle size measurement by optical microscopy, although it is not the only limitation on dimensional accuracy.

Electron microscopes surpass optical microscopes not only in overall magnification but also in greater depth of focus, while at the same time, on a different scale of dimensions,

are more susceptible to edge-location difficulties. As a rule of thumb, the depth of focus of an electron microscope is equal to the width of the field of view. At 1000 X, this corresponds to about 100 μm (compared to 0.5 μm for the optical microscope). At a typical magnification for particle size, e.g., 20,000 X, the depth of focus is on the order of 5 μm . The width of the blur-region in electron microscope imaging is correspondingly smaller but still significant in proportion to the size of the objects measured. For an SEM, the blur-region width is of the order of the electron-beam spot size, and can be as small as 5 nm in high-resolution systems or as large as 50 nm. The lower limit applies only in the case of transmission electron detectors. Edge location uncertainties of 10 nm and larger can be anticipated for secondary and backscattered electron detection. For a TEM, the blur-region width is on the order of 1-2 nm for ordinary instruments. Thus, while the optical microscope as described above has an edge-location ambiguity in width measurements of up to 0.5 μm , the electron microscopes have an ambiguity at least ten times less or about 0.05 μm for an ordinary SEM and about 2 nm for a not-unusual TEM.

The significance of edge-location ambiguity is this: similar objects measured with similar microscopes can have apparent sizes which differ systematically by as much as double the width of the blur region depending on the arbitrary choice of edge-location and focus setting alone. In an optical microscope, systematic differences of the order of 0.5 μm in size measurements could be attributed to just these effects. These are not errors inherent to the instrument but rather are systematic errors which are not removed by line-scale calibration. Other calibration techniques, involving either comparison to extended objects of known size or theoretical modeling of the image process, can reduce or eliminate these effects. This topic will be discussed more thoroughly in another section of the report.

As a note, for a number of reasons, including attempts to eliminate changes in polymer particle dimensions for certain PVC latexes due to evacuation and irradiation in electron microscopy [C20, D5] and also to reduce depth of focus problems in optical microscopy [C9], metal vapor deposition has been used to produce shadows of polymer spheres, where measurements are subsequently made on the circular openings in the deposited film rather than on the original polymer sphere [C9, C20, D5].

b. Non-imaging size phenomena

Apart from instruments which produce direct images, there are instruments which exploit other size-dependent phenomena for particle measurements. Most of these other phenomena involve the particles' radiation scattering properties, velocity, or volume displacement.

The volume-displacement type of particle-size instrument is the one which has been variously described as an electrical-sensing-zone [A3] or electrical-resistance [D11] particle counter. Such an instrument scales and counts the current pulses produced as individual particles pass sequentially through an aperture, on either side of which is an electrode, and thereby displace a volume of electrolyte through which current flows. Versions of the basic device were patented and first marketed by Coulter Electronics Inc. over two decades ago and have been available from at least six manufacturers in the U.S., West Germany, Japan, and Eastern Europe [A3, Appendix B].

In principle, the measured change in current due to the particles' presence between the electrodes is directly proportional to the volume of the fluid displaced which is identical to the volume which the material of the particle occupies. Allen devotes a textbook chapter to the instrument, reviewing the equation form $\Delta i \sim v(1 - a/A)^{-1}$, where v is the volume of fluid displaced, Δi is a change in current, and a and A are cross-sectional areas of the particle and aperture, respectively.

Allen reports that for spherical particles which are large compared to the aperture (particle diameter about 0.4 times aperture diameter), "the error involved in assuming a linear relationship is about 5.5%." He also reports "discrepancies of unspecified degrees between computed weight of particles counted and weight in suspension as being usually explained by differences between the envelope of the particle being measured, as opposed to the true volume."

Coincidence effects, which affect flow-through counters of both the light-blockage [W10] as well as the electrical-sensing-zone types, have been studied extensively as

indicated by the citations in, for example, Coulter's Industrial Bibliography* and Allen's text [A3]. Two types of coincidence errors are postulated: primary or horizontal coincidence due to two particles which give rise to two overlapping pulses; and secondary or vertical coincidence due to two particles below threshold which give rise to one pulse of a single large particle. Besides these error sources in counting, Allen (A3) covers the work of others and his own work on factors which distort the basic volume displacement proportionality [A3]. These factors include: the conductivities of the particle and electrolyte; the effective volumes of the aperture and the particle; the particle shape and its orientation during passage through the aperture; the presence of more than one particle in the sensing zone (coincidence); pulse shape dependence on wall effects and hydrodynamic focusing; and means of end-point determination.

Apparently, in practice, instrument response is independent of the resistivity of the particle and Berg, quoted in Ref. A3, suggest that this is due to the Helmholtz electrical double layer and associated solvent molecules at the surface of the particle.

While instruments involving electromagnetic scattering include examples such as x-ray, γ -ray, or ultrasound [see, for example, Refs. D8, D11-14], light scattering and specifically visible-light scattering are the most common instruments currently in use.

Similarly to the term particle-size, light scattering is an inclusive one that encompasses a broad range of instrumentation, techniques, and physical phenomena. In general, there is an incoming light beam incident on one or a collection of particles and a measurement of some property of the scattered outgoing light. The outgoing light, like the incident light, is characterized by amplitude or intensity, phase, frequency, direction of propagation and state of polarization. A theoretical model is used to relate some combination of these parameters of the scattered light to the size of the particle or particles doing the scattering. In some instruments, the relevant theory is explicit and detailed enough to provide a direct measurement of particle size, i.e., one in which the size is calculated directly from the basic mode; in other light-scattering instruments, the model is sufficient only to allow comparisons of particles of unknown size to those of known sizes. Because of their significance as potential candidate instruments for the calibration of particle reference materials, the function and theory of light-scattering instruments will be examined in more detail below in Section 3.B.

Instruments which determine particle-size via the measurement of size-dependent velocity of motion do so by various means. The means differ according to the cause of the motion and how the velocity is measured. The size-dependent velocity can be due to, for example: settling with buoyancy under gravity [C4, C5]; centrifugation or flow under pressure [D8, D11-13]; Brownian motion [R7, L13]; or forced-vibration of sinusoidal [S2] or non-sinusoidal types [S1]. The size-dependent velocity can be measured, for example, by: transit-times or separation due to velocity differences [D8, D11-13], doppler-frequency-shift [C4, C5], or time-correlation [L13, G10].

While some of these techniques and their variations use light, even scattered light, for the particle velocity determination, these techniques are distinguished from what is here called angular-intensity light-scattering because the size-dependent phenomena is principally described by aerodynamic or hydrodynamic equations for objects moving in fluids rather than by equations for electromagnetic waves scattered from spheres.

Velocity-dependent light-scattering as a means of particle size measurement, especially applied to liquid-drop aerosols, is well-established with a literature of its own. It includes the doppler-shift instruments and techniques variously described, for example, as: laser doppler velocimetry [F5], doppler shift spectroscopy [C4, C5, F4, H12, H13], or simply laser doppler systems [S1, S2, D22]. For the most part, these systems, with the exception of those of Refs. S1 and S2, deal with flow or settling. Where the particle velocity is due to Brownian motion, a related family of techniques includes those variously described, for example, as: photon correlation [C11, G10], homodyne [H14], optical self-beating [L13]; or Rayleigh-linewidth [R10] spectroscopy.

*Available from Coulter Electronics, Inc., Hialeah, Fla.

2.B.2. Number of Particles Involved

The number of scatterings involved in most light scattering techniques is usually a single one; that is, the light which reaches the detector has been scattered only once. Single-scattering is the basis of techniques which look at one isolated particle at a time in a single event [e.g., W15-W16], at one isolated particle at a time in a rapid series [e.g., W12], or at many particles at one time for single-scattering from multiple particles in parallel [e.g., R7].

2.B.3. Separation of Particles By Size

Another factor about particle-size instruments which bears on their performance as measuring devices is whether they involve intentional separation of particles by size. Such separation can be achieved in a number of ways, for example, mechanically, aerodynamically, or hydrodynamically.

Sieving is a technique for mechanically separating particulate matter into size intervals and is used both for mass-handling of tons of large particle materials and micro-handling of fine particle materials as small as $1\text{ }\mu\text{m}$ in size. For sieves with openings of known dimensions, the sieving operation is one of successive separations into groups smaller and larger than those which just fit through the openings. It is a conventional way of sizing standard glass beads and microspheres [H18, C22]. It gives a name to those particles smaller than those which can be satisfactorily sized by sieving; particles in the "sub-sieve" category [O1], however, can be larger than the smallest sized by sieving.

Impactor-sizing is a technique for aerodynamically separating particulate matter into size intervals; impactors are used most often for the characterization of airborne contaminants such as dusts and smokes. In such devices particulate matter is deposited on collectors according to the aerodynamic momentum associated with the particles. For a fixed velocity, separation by momentum corresponds to separation by mass, which for a known density corresponds to separation by volume, which for an assumed spherical shape corresponds to separation by diameter. Relatively recent designs for variable-slit [C24] and low-pressure [H7] impactors have provided a means to measure aerodynamic particle sizes over continuous or discrete ranges down to diameters of $0.05\text{ }\mu\text{m}$ or less.

Sedimentation and centrifugation are techniques for hydrodynamically separating particulate matter into size intervals and, most often in laboratories, are used for the smaller, $<1\text{ }\mu\text{m}$, particles [O1, D11-14]. In such devices the concentration of particles suspended at various depths is determined as a function of settling time. Concentrations are determined, for examples, by light [D12], x-ray [O1] or γ -ray [D12] attenuation at various depths or times.

2.B.4. Types of Dimensional Calibration

Instruments which measure particle-size do so by a comparison, indirect or direct, with the basic dimensional unit of length. This comparison requires explicitly or implicitly the use of some practical length standard, which can be a particle of known size, a linescale or a wavelength of light. Direct-imaging instruments can use any of the three; non-imaging instruments can use only the first and last.

a. Direct-imaging instruments

Electron and optical microscopes are usually calibrated for dimensional measurements by a ratio technique either using a linescale such as a stage micrometer or replica grating [e.g., in Refs. B16, R11, H4], or using particles of a known size [e.g., in Ref. H4, C8]. While each of the two approaches, linescale or particles of known size, follows the same procedure, there is a consequential if subtle difference in them which results in differences and varying degrees of dimensional errors. Where the magnification M_s of a microscope is calibrated by means of a linescale of known spacing S_0 , the measured dimension of the unknown, D_x , is given in terms of the dimensions of the images of the known spacing and the unknown particles, s_0 and d_x respectively:

$$(1a) \quad D_x (\mu m) = \frac{d_x (mm)}{s_o (mm)} S_o (\mu m), \text{ or}$$

$$(1b) \quad D_x (\mu m) = M_s^{-1} d_x (\mu m), \text{ where}$$

$$(1c) \quad M_s = \frac{s_o (mm)}{S_o (\mu m)} .$$

Where the magnification M_D of a microscope is calibrated by means of particles of known dimension D_o , the measured dimension of the unknown, D_x , is given in terms of the dimensions of the images of the known and unknown particles, d_o and d_x respectively:

$$(2a) \quad D_x (\mu m) = \frac{d_x (mm)}{d_o (mm)} D_o (\mu m), \text{ or}$$

$$(2b) \quad D_x (\mu m) = M_p^{-1} d_x (\mu m), \text{ where}$$

$$(2c) \quad M_p = \frac{d_o (mm)}{D_o (\mu m)} .$$

The analogous equations for the measurement of unknown line spacings in terms of known ones are:

$$(3a) \quad S_x (\mu m) = \frac{s_x (mm)}{s_o (mm)} S_o (\mu m), \text{ or}$$

$$(3b) \quad S_x (\mu m) = M_s^{-1} s_x (mm), \text{ where}$$

$$(3c) \quad M_s = \frac{s_o (mm)}{S_o (\mu m)} .$$

Equations 1a and 2a are usually implicitly and erroneously assumed to yield results identical to each other and to Eq. 3a. But because of the edge location phenomena described earlier, they can and do give greatly different results. Rearrangement of Eqs. 1a, 2a, and 3a into explicit ratios begins to show the basis for the differences which occur:

$$(4a) \quad \frac{D_x}{D_o} = \frac{d_x}{d_o}$$

$$(4b) \quad \frac{D}{S_0} \frac{x}{s_0} = \frac{d}{s_0} \frac{x}{s_0}$$

$$(4c) \quad \frac{S}{S_0} \frac{x}{s_0} = \frac{s}{s_0} \frac{x}{s_0}$$

Here it is at least formally explicit that calibration with particles of known size, as in Eq. 4a, consists of comparing widths-to-widths while calibration for particle measurements with a linescale as in Eq. 4b consists of comparing widths-to-spacings in dissimilar objects.

Calibration for spacing measurements with a linescale as in Eq. 4c consists of comparing spacings-to-spacings.

It has been demonstrated that in an optical microscope, the apparent width of an object's image depends on the edge location criterion, focussing, and instrument operating conditions [C9, N5, S11-12]. Further, it has been demonstrated, for both spherical particles [C9] and planar objects [S12], that the apparent width d' can differ from the geometrical-optical width d by an increment Δ which depends on edge-location criteria, etc., but is relatively constant over a range of object sizes (e.g., from 0.2 to 2 μm [Ref. C9] and similarly 1 to 10 μm [S12]). Thus,

$$(5a) \quad d' = d + \Delta.$$

In the same imaging systems, the apparent spacings of a linescale are in practice to a very high degree free of these effects and in principle are independent of them [S11, S12]. Thus,

$$(6) \quad s' = s.$$

Substitution of Eqs. 5a and 6 as appropriate into Eqs. 4a-4c results in expressions for the ratios of object and image dimensions.

$$(7a) \quad \frac{D}{D_0} \frac{x}{s_0} = \frac{d + \Delta}{d_0 + \Delta} \frac{x}{s_0}$$

$$(7b) \quad \frac{D}{S_0} \frac{x}{s_0} = \frac{d + \Delta}{s_0} \frac{x}{s_0}$$

$$(7c) \quad \frac{S}{S_0} \frac{x}{s_0} = \frac{s}{s_0} \frac{x}{s_0}$$

For a difference in size between the known and unknown particles of Eq. 7a given by $d_x = d_0 + \delta$ and for a geometrical-optical magnification M given by Eqs. 1c through 3c, the difference in the object size corresponding to the difference between the apparent and the geometrical-optics image size, becomes for the three cases shown in Eqs. 7a-7c:

Case I. Particles of unknown size measured by ratio to particles of known size.

$$(8a) \quad \epsilon = D_x - \frac{d}{M} \frac{x}{M} = \frac{\Delta}{M} \cdot \frac{\delta}{d_0} .$$

Case II. Particles of unknown size measured by ratio to lines of known spacings.

$$(8b) \quad \epsilon = D_x - \frac{d}{M} \frac{x}{M} = \frac{\Delta}{M} \cdot (1) = \frac{\delta}{M} .$$

Case III. Lines of unknown spacing measured by ratio to lines of known spacing.

$$(8c) \quad \epsilon = S_x - \frac{s}{M} \frac{x}{M} = \frac{\Delta}{M} \cdot (0) = 0 .$$

Eqs. 8a, b, and c can be used to examine how systematic error which can arise in microscope measurements of dimensions due to ambiguities in image edge location is affected by various calibration techniques. The basis for such errors is the distance $\Delta/2$ between the apparent edge of an object's image and that determined by geometrical (electron or light) optics; the corresponding ambiguity for the object edge is $\Delta/2M$ and for the object width Δ/M . Based on the discussion earlier, Δ/M can be of the order of $0.25 \mu\text{m}$ or more for an optical microscope [e.g., in Refs. C4, S11, and 12] while for an electron microscope, the author would anticipate Δ/M to be of the order of one-tenth that amount or $0.01 \mu\text{m}$ or so for an ideal object.

Given a non-zero Δ/M then, in a measurement of an unknown linespacing against a known one, the error due to edge location as represented by Eq. 8c is zero. In a measurement of an extended object, either against a similar extended object or against a linespacing, the error due to edge location as represented by Eqs. 8a and 8b is non-zero. For calibration with a linescale, the error in the dimensions of a particle could be on the order of $0.25 \mu\text{m}$ for an optical microscope measurement and on the order of $0.02 \mu\text{m}$ for a scanning electron microscope measurement independent of particle size (based just on considerations of what goes on in the image plane; other effects can mitigate or compound these errors). For calibration with particles of known size, the error depends also on the difference in size between the unknown and known particles. For example, in the measurement of an (unknown) $15 \mu\text{m}$ particle against a (known) $10 \mu\text{m}$ particle, the error in size according to Eq. 8a for an optical microscope measurement might be:

$$(9) \quad \epsilon = 0.25 \left(\frac{10-15}{10} \right) = 0.125 \mu\text{m}$$

and for an electron microscope measurement:

$$(10) \quad \epsilon = 0.02 \left(\frac{10-15}{10} \right) = 0.01 \mu\text{m}$$

while for a measurement of a $10.1 \mu\text{m}$ (unknown) against a $10 \mu\text{m}$ (known) the respective errors might be:

$$(11) \quad \epsilon = 0.25 \left(\frac{10.1-10}{10} \right) = 0.025 \mu\text{m} .$$

Both the formal relationships of Eq. 8a, b, and c and the numerical examples just given illustrate some major points about the calibration of microscopes for dimensional measurements. First, there is sound evidence that edge-location ambiguities should lead one to anticipate systematic errors on the order of many tenths of a μm in optical microscope measurements and on the order of a hundredth of a μm in electron microscope measurements of the dimensions of extended objects such as particles. Second, these errors can be reduced, but not eliminated, by calibration against known spheres and only if the knowns and unknowns are close in size. Since these errors depend on the specific means by which an imaged apparent edge is located with respect to the geometric edge, one further way to deal with them is via a theoretical model of the microscope and its interaction with the object, a model which quantitatively describes the relation between the image profile and the object. In formal terms such a model mathematically describes, for example, the (light or electron) intensity distribution within the image as a function of position x and variables of the instrument, e.g.

$$(13) \quad I = I(x, \alpha, \beta).$$

Such a model and a linear displacement measuring device allow scanning of a microscope image and the location of the intensities, I_g , corresponding to those determined by geometric optics. The measured width of an object corresponds then to the distance between the points on the image at those intensities:

$$(14) \quad w = x(I_1) - x(I_2).$$

The displacement measuring device for such a measurement can be a calibrated transducer [N5] or an interferometer which can relate the measurements directly to the wavelength of light [S13].

b. Non-imaging instruments

While imaging instruments can be dimensionally calibrated by linescales (or displacement-measuring devices), non-imaging are usually calibrated by one or the other of the two remaining methods: explicit comparison of particles against other particles of known size or implicit comparison against a wavelength of light.

Commercial flow-through counters of the volume-displacement type [C25], the light shadow-projection type [W10], or other light-ratio types [W12] are calibrated using particles of known mean size and size distributions. Some commercial single-particle light scatter instruments of the levitation [W15] or flow-through type [W18] compare against the wavelength of the light source. Most laser light-scattering instruments, including those which scatter light from suspensions [D11-14, W12, G1] as well as the single-particle types just mentioned, make implicit comparison against the light wavelength which appears as an input parameter to a theoretical-analytical calculation of instrument response.

For angular-intensity light-scattering instruments, the calculation involves complex equations requiring computer numerical evaluation techniques. As such, no simple descriptive form of the dependence of intensity I vs. angles θ and ϕ , particle size d , and light wavelength λ and complex index of refraction m can be given. Formally, however,

$$(15) \quad I = I(\theta, \phi, x, m, \dots)$$

where the size parameter $x = \pi d/\lambda$ and d is the diameter of the spherical particle. Here the comparison of particle size vs wavelength is calculational direct.

In particle-velocity light-scattering instruments, the calculation, in special cases, can be independent of angular-intensity theory and involve only hydrodynamic motion theories: for example, in first-order calculations, measurements on collections of particles of

nearly identical size [C4]. The most analytically simple case will demonstrate a point about dimensional calibration against the wavelength of light in velocity systems. For example, for particles following Stokes behavior, the viscous force F is given by

$$(16) \quad F = 6\pi\eta a v$$

where a is particle radius, η is the viscosity, and v is the particle velocity. A more specific example is for spherical particles of density, ρ , settling under gravity g , at terminal velocity in air, where the viscous and gravitational forces are equal and

$$(17) \quad 6\pi\eta R v = \frac{4}{3} \pi R^3 \rho g$$

and

$$(18) \quad v = \frac{2\rho g R^2}{9} .$$

For a Doppler shift given in terms of the vector velocity v and the light propagation vector k :

$$(19) \quad f = \frac{1}{2\pi} v \cdot k$$

where

$$(20) \quad |k| = \frac{4\pi\eta_{\text{air}}}{1} \sin \frac{\theta}{2} .$$

Combination of the Stokes and Doppler equations gives the measurable frequency shift of the scattered light as a function of the particle size r and the wavelength of the light λ , as well as other system variables:

$$(21) \quad \Delta f = \frac{1}{2\pi} \left(\frac{2\rho g}{9} \right) (4\pi\eta_{\text{air}}) \sin \frac{\theta}{2} \frac{r^2}{\lambda}$$

or

$$(22) \quad f \sim \frac{r^2}{\lambda}$$

The most significant point to be made concerns dimensional calibration, and is that while the particle size in aerodynamic or hydrodynamic velocity measurements is determined in terms of the wavelength of light, it is done in a way different than in angular-intensity light scattering where the size information and dimensional calibration is in the scaling parameter $x = 2 \pi r / \lambda$.

Calibration of flow-through counters against particles of known size can be accomplished in at least two ways: a single-point (one ratio) technique and a multiple-point (two or more ratio) technique. A single-point technique can accommodate scale-factor (i.e. multiplicative) effects if no off-set (i.e. additive) effects are present. In the presence of off-set effects, at least a two-point calibration is required. Some models of commercial flow-through counters of both light-blockage and electrical-sensing-zone types can be adjusted in at least two-point calibrations. Further, there is a technique for determining

the fraction of the total particles in a sample which are smaller in size than that which can be detected, sized, and counted [A3].

2.C. Single-Number Index to Characterize Particle Dimensions

Individual particles of matter are three-dimensional objects and dusts, powders, and suspensions are collections of vast numbers of individual particles. The determination of a characteristic particle size for a collection of particles therefore involves defining and measuring a size of one particle and defining and measuring a size of a population of particles.

2.C.1. Characterizing a Single Particle

An individual particle is a real three-dimensional object which has no one unique dimension which to call its size. As a geometrical object it is complex and irregular. As an object-to-be-measured, it is the receiver of action in one of many operational definitions where other operational definitions yield other sizes because they treat other geometrical representations of the particle. Most often the geometry is described in terms of the diameter of an equivalent circle or sphere; a sample of twelve such diameters with their definitions is listed in Table 3.

Microscopes, both optical and electron, and one type of flow-through counter [W10], measure particle size by scaling a two-dimensional plane projection of the three-dimensional particle. In a microscope, a non-circular image can be characterized in various ways: Feret's diameter d_F which is the distance between parallel tangents to the outline of the projected image; Martin's diameter, a mean chord length; or, one not shown in Table 3, a shear diameter, d_S , which is obtained with an image splitting eyepiece and is the Feret's diameter parallel to the eyepiece axis independent of the particle orientation [S10]. In the light-blockage type of particle counter, the particle size is given as the diameter d_{pMAX} of the circle equal in area to the maximum projected area of a tumbling particle [W10]. Note that maximum projected area diameters d_{pMAX} differs from the random-orientation projected area diameters, d_{pr} , the latter being for a particle lying on a substrate in a microscope. Besides being characterized in terms of a straight line chord-type dimension or an area-type dimension, projected plane images can be characterized by their perimeter.

Electrical-sensing-zone particle counters and one special-type of light scattering instrument measure particle size in terms of the individual particle's volume. For the former, the effect is the volume of liquid electrolyte displaced [C25]; for the latter, the effect is the Rayleigh scattering in which an electronic polarizability gives rise to a dipole moment proportional in strength to the volume of the particle [A3].

Hydrodynamic and aerodynamic velocity-dependent particle-size measuring devices, ranging from Doppler-shift spectrometers [C4] to precipitation impactors [C24, A7], measure particle size via Stokes'-type equations which involve volume-surface phenomena. The linear dimension in a Stokes-equation of the form: $\text{force} = (\text{shape factor}) \times (\text{dimension}) \times (\text{velocity})$ appears as the result of evaluation of complex-boundary conditions integrated over the surface of the object moving in the fluid [A3]. Further, where terminal velocities such as those due to gravity are measured, the Stokes force is equated to a buoyant force which is proportional to volume displacement:

$$(\text{gravity}) \times (\text{density}) \times (\text{volume}) = (\text{shape}) \times (\text{dimension}) \times (\text{velocity}).$$

Solution of this form of equation for a specific object shape yields the size vs velocity equation upon which size measurements are based. Other size-dependent phenomena which involve surface effects, such as gas adsorption, are used in commercial and laboratory-prototype devices [D11-14, D8, A3].

In almost all particle measurements, and independent of the physical phenomena and geometrical effects involved, the resulting single-number characterization of the non-ideal irregular, three-dimensional particle is given as the diameter of a(n) (equivalent) sphere. Where the particle is perfectly spherical, many of the geometrical effects would in form be the same - for example, the plane projection of a sphere is a circle whose diameters, whether

Table 3

Definitions of Particle Size [A3]		
Symbol	Name	Definition
d_v	Volume diameter	Diameter of a sphere having the same volume as the particle
d_s	Surface diameter	Diameter of a sphere having the same surface as the particle
d_{sv}	Surface volume diameter	Diameter of a sphere having the same external surface to volume ratio as a sphere
d_d	Drag diameter	Diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and at the same velocity (d_d approximates to D_s when Re is small)
d_f	Free-falling diameter	Diameter of a sphere having the same density and the same free-falling speed as the particle in a fluid of the same density and viscosity
d_{st}	Stokes' diameter	The free-falling diameter of a particle in the laminar flow region ($Re < 0.2$)
d_a	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle resting in a stable position
d_p	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle in random orientation
d_c	Perimeter diameter	Diameter of a circle having the same perimeter as the projected outline of the particle
d_A	Sieve diameter	The width of the minimum square aperture through which the particle will pass
d_F	Feret's diameter	The mean value of the distance between pairs of parallel tangents to the projected outline of the particle
d_M	Martin's diameter	The mean chord length of the projected outline of the particle

Feret or Martin's or image-shear, is the equatorial diameter. The diameter of the projected area in a maximum, random or stable orientation is the same diameter, as is the diameter of the sphere of equivalent surface area.

Two points are worth keeping in mind in the evaluation and intercomparison of experimental measurements on real particles, especially nearly-spherical real particles. One point is that particles are spherical only in relation to an individual technique's ability to detect deviations from sphericity. The second point is that even highly spherical particles have different equivalent spherical diameters according to the physical phenomenon and operational definition by which the various diameters are measured. A particle does not have a simple "true size" or an "absolute diameter" but rather these operationally defined sizes. Increases in precision can reveal systematic differences between variously-defined sizes while at the same time refinement and sophistication in theoretical modelling can produce convergence. Later in Section 4 on the intercomparison of particle sizes measured by various techniques, both the presence of systematic differences and the possibility of obtaining convergence will be apparent.

While this report is concerned primarily with spherical particles which can potentially serve as sized standard reference particles, Table 4 is given to illustrate some shape factors or coefficients and their definitions [A3, S10]. The factors have practical importance, especially in dealing with industrial powders, suspensions, dusts and atmospheres which are made up of irregularly-shaped particles. For spherical particles, the factors and coefficients reduce to unity or appropriate multiples of π .

As a practical matter, deviations from sphericity at even a low-level have a consequence on the precise determination of the mean size and population standard deviation (monodispersity) of highly spherical standard particles. Some observations that have been made about shape effects are worth keeping in mind in the evaluation of systematic error effects in the calibration of standard particles. In electron microscopy, the shape of the equatorial plane of the particle in a stable rest position on a substrate is viewed; and apparent particle shape can be changed by pin-cushion, barrel distortion, and related astigmatic effects on the two-dimensional imagery. Further, some evidence has been given that latex particles may distort in shape upon electron irradiation [T1]. In light scattering, the basic Mie theory only describes scattering from perfectly spherical objects [B11, K7, V4]. Techniques for dealing with light-scattering from nearly spherical particles such as oblate and prolate spheroids [A6, L3] and ellipsoids [L5] treat deviations from sphericity as perturbations on complex mathematical formulations [B11, K7, V4]. In flow-through particle counting of either the light-obscuration [C1, W10] or electrical sensing zone types [C25], particle shape determines the apparent size, changing the form and location of the size distribution curve for non-spherical particles relative to that for spherical ones [A3, W10]. The probable effect of a particle's asphericity on a measurement, whether by electron microscopy, light scattering, or flow-through counting, is to increase the apparent width of the size distribution, increase the uncertainty in the mean size, and shift the apparent mean size to some degree as well.

2.C.2. Giving an Average Size to a Group

Commercially and environmentally important microscopic particles occur seldom, if ever, individually or in small numbers having practically equal sizes, but instead occur in groups of great numbers having measurably different sizes. The common practical requirement that such a complex system be describable by a single index is reflected in the wish to characterize that population of a large number of irregularly-shaped, three-dimensional particles by one number, that is, by some average particle size. While the problem of defining a size of an individual particle is geometrical-physical, the problem of defining an average size for a population is statistical-physical.

A conventional manner of describing, with one number, a population of particles having different sizes is by means of a particle size distribution function. In tabular, graphical, or equation form, the size distribution describes the amount of particulate matter which occurs for a given size or size interval. The amount can be given in terms of mass; thus there is a number size distribution and a mass size distribution. Either distribution, by mass or number, can be characterized by an arithmetic average (or arithmetic mean) size d_a , by a geometric mean (or geometric average) size d_g , by a median size d_m , or by other

Table 4

Table of Shape Factors and Shape Coefficients [A3]		
Shape Factors	Definition	Coefficients
Sphericity	The ratio of the surface area of a sphere having the same volume as the particle to its actual area; the reciprocal is known as the coefficient of rugosity or angularity	$\psi = \frac{d^2}{d_s^2}$ $\psi < 1$
Circularity	The ratio of the perimeter of a circle having the same area as the projected area of the particle to its actual perimeter	$\chi = \frac{d}{d_c}$ $\chi < 1$
Surface-shape coefficient	Coefficient of proportionality relating the surface area of the particle with the square of its measured diameter	$S = \alpha_{s,A} d_A^2$
Volume-shape coefficient	Coefficient of proportionality relating the volume of the particle with the cube of its measured diameter	$V = \alpha_{v,A} d_A^3$
Surface-volume shape coefficient	Ratio of surface to volume shape coefficient	$\alpha_{s,v,A} = \frac{\alpha_{s,A}}{\alpha_{v,A}}$

Table 5

Mathematical Expressions of Various Mean Diameters of a Distribution		
Number-length mean diameter	$x_{NL} = \frac{\Sigma dL}{\Sigma dN} = \frac{\Sigma x dN}{\Sigma dN}$	
Number-surface mean diameter	$x_{NS} = \sqrt{\left(\frac{\Sigma dS}{\Sigma dN}\right)} = \sqrt{\left(\frac{\Sigma x^2 dN}{\Sigma dN}\right)}$	
Number-volume mean diameter	$x_{NV} = \sqrt[3]{\left(\frac{\Sigma dV}{\Sigma dN}\right)} = \sqrt[3]{\left(\frac{\Sigma x^3 dN}{\Sigma dN}\right)}$	
Length-surface mean diameter	$x_{LS} = \frac{\Sigma dS}{\Sigma dL} = \frac{\Sigma x^2 dN}{\Sigma x dN}$	
Length-volume mean diameter	$x_{LV} = \sqrt[3]{\left(\frac{\Sigma dV}{\Sigma dL}\right)} = \sqrt[3]{\left(\frac{\Sigma x^3 dN}{\Sigma x dN}\right)}$	
Surface-volume mean diameter	$x_{SV} = \frac{\Sigma dV}{\Sigma dS} = \frac{\Sigma x^3 dN}{\Sigma x^2 dN}$	
Volume-moment mean diameter	$x_{VM} = \frac{\Sigma dM}{\Sigma dV} = \frac{\Sigma x^4 dN}{\Sigma x^3 dN}$	
Weight, moment mean diameter	$x_{XM} = \frac{\Sigma dM}{\Sigma dW} = \frac{\Sigma x dW}{\Sigma dW} = \frac{\Sigma x^4 dN}{\Sigma x^3 dN}$	

types of averages or means based on either number or mass, as will be discussed later. In some cases, the distribution is characterized by a mode size.

The differences among mean, median, and mode values of particle size are of practical metrological importance. Most measurement processes and calculations yield one of many types of mean size, as will be discussed shortly; a recommended way of calibrating flow-through counters employs a median size; and at least one manufacturer of standard reference particles characterizes them in terms of a main-mode size. The use of a median or a mode requires an explicit graphical representation of the size distribution, such as a histogram.

If the distribution of sizes shows a peak, that is, if some size d_1 has more particles occurring at it than at nearby sizes above and below it, the size with more particles is a mode and the distribution is modal. Some processes produce particles which have a dominant single mode as, for example, batch grown latex particles. In contrast, other processes, such as vibrating-orifice generators, have been observed to produce particle distributions with two, three, or more modes [C4]; droplet-grown latex particles with tri-modal distributions have even been reported by manufacturers.

Some natural and industrial processes result in well-behaved single mode distributions which are symmetric and monotonically and asymptotically approach zero at sizes well above and below the modal size. For narrow-distribution particles such as polymer spheres, the distribution is symmetric in the linear dimension and can be described well for most applications by the Gaussian or normal distribution [A3]; for many ground or milled powders and glass beads, the distribution is symmetric in the log of the dimension and can be described by the log normal distribution [G2]; certain sub-0.1 μm polymer sphere distributions have been best described in hydrodynamic studies by symmetric but non-Gaussian distribution functions [C11].

The most commonly used mathematical distribution function is the Gaussian or normal distribution and its explicit use or implicit applicability is conveyed by the term "standard deviation" as the index of the width of the distribution. The standard deviation is the limiting value of the root-meansquare (RMS) average deviation of an infinitely large, normally distributed population. In metrology the standard deviation is a measure of the random scatter in measurement data, while in common usage in particle-size measurement, the standard deviation is a measure of the distribution of sizes in a population. Failure to clearly distinguish the variations associated with the measurements from the variations associated with the particle population can be troublesome and misleading.

In a measurement process statistical control is a must to yield valid results, and the variations in measurements are random and characterizable by a standard deviation σ_m . In a particle population with a normal distribution of sizes, that variation among sizes is characterized by a standard deviation σ_p . In a first order model of the results of applying the in-control measurement process to the normally-distributed particle population, the standard deviation σ_t of measurements on the population will be the quadrature combination of the two:

$$(23) \quad \sigma_t^2 = (\sigma_p^2 + \sigma_m^2)^{1/2}$$

for measurements on N particles, the standard deviation on the mean of the measurements will be:

$$(24) \quad \sigma_m = \frac{1}{N} \sigma_i^2 = \frac{1}{N} \left(\frac{1}{N-1} \sum (x-\bar{x})^2 \right)^{1/2}.$$

Given that σ_t is an observed scatter in measurement results, σ_m is the component of that scatter due to variations in size among the particles in the distribution, and σ_p is the component due to variations in the measurement process itself, some caution in interpreting results is required. For example, if one measures the apparent diameters of a

great number of particles as images on TEM plates and computes an RMS average deviation from the mean diameter, one obtains an estimate of σ_t . Without moving, refocusing, reimaging, and remeasuring one single unvarying particle to obtain an estimate of σ_p , one cannot determine σ_m , the quantity of interest.

The two equations above formally illustrate two points about measurements of particle size distributions. First, Eq. 23 shows that a standard deviation σ_t computed from measurement data for a distribution of particles is equal to the particle distribution standard deviation σ_p only in the limit of small measurement uncertainty, or:

$$(25) \quad \sigma_t \simeq \sigma_p \text{ if and only if } \sigma_p \gg \sigma_m .$$

Since σ_m can be determined only by a separate determination, such as by repeated measurements on one particle, the assumption that $\sigma_p \gg \sigma_m$ should be questioned. However, given the absence from the literature of data upon which estimates of the variability σ_p for the different measurement techniques, one can only keep the difference between σ_t and σ_m in mind and treat σ_t as an upper limit for σ_m . As a second point, since the effective number of particles N involved in multiple-particle phenomena (such as that seen in many forms of light-scattering) is not known, the uncertainty in mean particle size cannot be easily reduced without separate redeterminations. Further, the assumption of a normal distribution of particle sizes for real populations of particles should be made with reserve.

Caution and special mathematical techniques are also required to deal with multi-mode or unsymmetric, skewed distributions [A3]. An expediency is to treat the dominant mode as a single mode, ignoring parts of the distribution. Number averages are most susceptible to the biasing effect of small particles which can occur in large numbers and would be counted in one technique and would go undetected or intentionally uncouned in another technique; mass averages are most susceptible to the biasing effect of large particles which carry proportionally so much more mass than many small particles.

While number-average and mass-average mean diameter are most commonly used, they are only two of the many moments of a distribution which can be computed and which find use.

Table 5 shows eight such moment-mean diameters, with their general and specific expressions for spherical particles. In general these moment-means are of the form:

$$(26) \quad w_{\text{mean}} = \frac{\text{sum (number x weighting factor \#1 x size)}}{\text{sum (number x weighting factor \#2)}}$$

where the sum is over the sizes or intervals, the number is the number of particles for a given size or interval, and the weighting factors are geometrical factors such as length, area, volume, or weight. The physical and formal differences among these various mean diameters is of metrological consequence since different particle-size measurement techniques, either inherently or by convention or convenience, determine different types of mean diameters; for example, microscope measurements of diameters lead directly to a number-length mean diameter; certain light-scattering techniques including extinction and laser-Doppler velocimetry yield a number-area mean diameter; and mass-deposition devices, such as impactors yield a number-mass (or weight) mean diameter.

Part II of this report, now concluded, has been an overview of those elements of particle-size measurement systems which contribute significantly to the measurement process and produce a number called a particle size. The particles of central interest to this report are those which are spherical and monosize. The measurement techniques of central interest are the three techniques by which such particles can be dimensionally calibrated in a consistent and compatible scheme.

3. CANDIDATE INSTRUMENTS FOR STANDARDS CALIBRATION

A. Needs of Calibration Scheme

The needs and capabilities of industry and science with regard to sized particle reference materials place stringent demands on the method of calibration in regard to the dimensional measurements by which the particles are calibrated and their size is certified. The measurements must be definitive in the sense that they are accurate to a degree commensurate with users present and near-future capabilities. In more specific terms, this means that a calibration technique must yield high-resolution measurements of some defined particle size, and still, to a high degree, be independent of time and technique. Besides being accurate, the techniques also need to be reasonably fast and economical.

No single current measurement technique meets all these general requirements. Electron microscopy can provide high-resolution, unambiguous imaging and dimensional measurement of even sub-0.1 μm individual particles. It can provide direct-image information on particle shape and surface features and on the presence of agglomeration or debris. It can provide via image-analysis of either manual or automatic form, an explicit histogram of particle size distribution. However, it has the disadvantages that it is slow, necessarily involves limited sampling of the population, and subjects the particles to vacuum and electron irradiation.

Light-scattering from a suspension can provide high-resolution, dimensional information averaged over a large number of particles in their normal environment. The method is fast, non-intrusive, and can provide mean size and population standard deviation. It is advantageous in that it is based on a well-established theory. But the method is model-dependent and requires prior knowledge or assumptions, usually that the particles are spherical, homogenous, normally-distributed in size, and have a certain index of refraction. Also scattering from a suspension cannot well distinguish agglomeration or debris or deviations from sphericity.

Flow-through liquid-borne particle counters can provide moderately high resolution, and fast, sequential measurements of individual particles in a sample of a liquid suspension. They can provide an explicit, built-up histogram and so distinguish normal distributions from skewed or multimodal ones. They also are comparators which require particles of known size for their calibration, with the lower limit of the range of commercial devices at about 0.5 μm . The electrical-sensing zone type requires that particles be in an electrolyte solution. This type and the optical type involve consumption of the sample, and although they cannot distinguish debris, they do give evidence when agglomeration occurs.

While other particle-size measurement techniques are available, the three aforementioned complement each other in a scheme which promises to provide measurements which are accurate, fast, economical, and independent of method to a degree sufficient to meet the needs of today's seekers of sized standard reference particles.

Because both electron microscopy and certain forms of light-scattering are direct-measurement techniques (that is, they yield dimensional measurements of particle size without requiring particles of known size for comparison), each could be a primary calibration technique in its own right. However, because the two techniques involve independent operational definitions of particle size which do not necessarily yield corresponding results, intercomparison and refinement of the techniques, theoretical models, mathematical algorithms, and formal definitions to achieve such correspondence may be required. Flow-through counters could then provide more information for the refinement process and be used for a rapid, convenient, secondary calibration in which particles of unknown sizes are calibrated by comparison against particles of known sizes from a primary calibration. In this context, these three generic techniques will now be examined in more detail.

B. Interrelationships of Three Candidate Measurement Methods

3.B.1. Electron Microscopy

In electron microscope measurement of particle size, electrons from a source are focused via electron optics onto the particle and either electrons transmitted and attenuated

by the particle (as in a TEM) or "reflected" (actually either backscattered electrons or different secondary emission electrons) by the particle as in an SEM are imaged. In a TEM the imaging is usually done directly onto an electron-sensitive photographic plate; in an SEM the imaging is done by detecting the electrons and forming an image on a cathode-ray tube where intensity is proportional to the current detected. TEM requires a measurement of the directly-exposed image on the plate, usually done visually with a reticle or with some form of semi- or fully-automated image analyzer. SEM requires a measurement of either an image on a photograph of the CRT screen or some form of scaling of the electron intensity profile. In general, analytical models of the imaging process are not used and apparently not thought to be required.

Early innovative work on electron microscope measurements of polymer sphere diameters was done by Bradford and Vanderhoff at Dow in 1954 [B16]. Bradford has continued to the present [R11] work which is the basis for the mean particle sizes attributed to the more than sixty Dow latexes marketed since 1947 [B2].

The basic technique, apart from some changes in instruments and calibration materials, has been unchanged [R11]. At the heart of the technique is the measurement of the apparent diameter of the TEM image of a particle against the apparent spacings of the TEM image of the lines of a replica grating upon which the particle rests. In the 1954 paper, the authors report using a shadowed silicon monoxide replica grating with 1134 lines per mm mounted on a stainless steel grid. The choice of the silicon monoxide stainless steel combination was made after they observed that collodion shrank 5% after five minutes of irradiation and that in a similar period 0.34 μm polystyrene spheres on collodion replica on a copper grid could grow in size by 15% (0.007 μm). In that report the effects and levels of beam current, contamination growth, and pumping rate were not known.

In the 1979 paper, the author reports using a new instrument with a shadowed carbon replica grating of 2160 lines/mm. By private communication he reports that particles to be measured are air-dried on the replica grating, evacuated to 10^{-5} Torr, and irradiated with 50 Kev electrons at magnifications of 7000X - 20,000X; the resulting photographic plate shows particle images 1-4 mm in diameter against a background showing about nine lines of the grating replica. The apparent diameters of the particle images and apparent spacings of the grating are measured visually with an eyepiece magnifier to a precision of about ± 0.02 mm. A range of from 70 to 300 particles are measured and the mean and standard deviation are calculated directly from the data. A typical standard deviation is ± 0.005 μm for particles in the range 0.1 to 1.0 μm , independent of mean size, and the standard deviation is attributed wholly to the distribution in particle sizes, on the apparent premise that the standard deviation of the measurement is much smaller than that of the particle size distribution. In 1979, the mean diameter of the Dow LS-1028-E latex, previously measured by Dow and found to be 1.099 μm , was remeasured by them and reported without comment to be 1.192 μm [R11].

In the last few years, independent and sometimes very thorough electron microscope measurements on polystyrene spheres and Dow latexes in particular have been reported by various workers [A4, C11, C20, C23, D3, D6, D20, H4]. Of these, some data from comparisons by Davidson and Haller [D3], Heard [H4], Dobbins [D21] and Davidson, et al. [D6] will be examined in some detail later in this report. For the moment, two of the reports of work, which like that of Bradford [B16], systematically investigated error effects in TEM measurements of particle-size, will be described in brief.

Heard, et al., measured mean particle sizes of nine Dow latexes and reported results in a paper entitled "A Redetermination of the Diameters of Dow Polystyrene Latexes" [H4]. They reported that they used a carbon replica grating, 300 Å thick, gold-palladium shadowed, having 30,000 lines per inch (1181 lines per mm), and mounted on copper 200 mesh grids. To minimize radiation damage to the spheres, measurements were made at 100 Kev accelerating voltage at the lowest beam current giving acceptable images with three second exposures. To minimize contamination, a cold-finger stage was used. For 0.5 to 1 μm spheres, the TEM magnification was 10,000 to 20,000X while for 0.3 to 0.8 μm spheres the magnification was 30,000 to 50,000X. A measurement at 12,500X on the screen gave 25,000X on the photographic print, and on such a print the apparent diameters of images of latex spheres was 17 to 28 mm against an apparent spacing of 20 mm for six grating lines on the print. Diameters and spacings for images on print were measured with a reticle to precisions of ± 0.2 mm.

Among other effects, Heard reported that fidelity of reproduction of the replica grid was demonstrated by direct measurement ($29,900 \pm 100$ lines/inch measured for replica compared to 30,000 quoted for the master by the manufacturer). In addition, there was no detectable change in replica grating spacing on irradiation ($<0.2\%$ change in 10 min.), and no detectable change in sphere size on irradiation at normal beam currents. However, $1\text{ }\mu\text{m}$ spheres decreased in size by 2% in the first minute and 5% in 10 minutes at beam currents of four times normal, corresponding to magnifications of twice normal; the decrease was about half as much for $0.1\text{ }\mu\text{m}$ spheres.

In Heard's measurements of particles against replica gratings and against other particles in a ratio technique, it was quoted that there were estimated total uncertainties (1σ) of $\pm 0.008\text{ }\mu\text{m}$ for $0.365\text{ }\mu\text{m}$ particles up to $\pm 0.016\text{ }\mu\text{m}$ for $1.16\text{ }\mu\text{m}$ particles. These variations were attributed wholly to the measurements and not at all to the particle population.

Davidson and various co-workers, in allied papers [D2-7], performed measurements on various polystyrene latexes (including Dow latexes) using various techniques, including light-scattering and electron microscopy. One paper by Davidson and Haller, entitled "Latex Particle Size Analysis: V. Analysis of Errors in Electron Microscopy", deals systematically with the subject [D3]. Among the effects experimentally measured were those due to grid material, ion exchange of the latex, vacuum conditions, magnification variation over time, method of measuring the photographic images including filar eyepiece and spot-projecting image analyzer, and image reproduction by contact print and enlargement.

Among other conclusions, Davidson and Haller decided the following: neither grid type nor ion exchange "had much effect" on measured diameters; the effects of irradiation and pumping rate were negligible if micrographs were made within one minute of initial beam exposure; changes in pumping rate could cause apparent particle diameter to increase, decrease, or remain constant with beam exposure; sizing of images by means of a filar micrometer eyepiece gave diameters "very close to those from other methods"; the projected-spot image analyzer (Zeiss TGZ-3) gave results comparable to the filar if enlarged transparencies were counted which showed the latex particles as black dots against a white background; and if negatives were counted directly (white dots against black background), the diameters so obtained were often lower than those obtained by filar counting. Finally, it was concluded that "the magnitude of the various errors in electron microscopy of polystyrene latex for sharp negatives" is at the 90% confidence level $\pm 3\%$ in magnification, $\pm 3\%$ on average diameter of sample, $\pm 3\%$ for filar micrometer sizing, $\pm 5\%$ for Zeiss TGZ-3 sizing of 5 mm black spots, and the combined total error is approximately 5% for filar counting and 7% for the projected-spot counting.

On the important issue of changes in the diameter of polymer latex spheres during exposure to the electron beam in an electron microscope, the evidence is not overwhelming but seems to indicate that polystyrene latex spheres can be measured with a negligible (but unspecified) change in size if the exposure is at a low beam current and brief. Early on, Davidson and Haller [D3] reported that the apparent size could increase, decrease, or remain the same depending on pumping rates; they speculated that a no-change situation corresponded to a balance between diameter decrease due to mass loss and diameter increase due to contamination deposition. Talmon and Miller [T1] reported that while "soft" latexes, such as benzene-plasticized polystyrene, required special techniques such as an $85\text{ }^\circ\text{K}$ cold stage and embedding between polyimide sheets, "glassy" latexes such as unplasticized polystyrene could be measured well just by spraying, drying, and normal handling. Similarly, Claver and Farnham [C20], while reporting decreases in diameters of polystyrene spheres of from 2 to 9% upon intense exposure for many minutes, conclude that "a maximum (mass) loss from polystyrene is negligibly small for all but the most precise measurements". Finally, Heard, et al. [H4], in the most explicit statement of the magnitude of the effect for normal exposures lasting up to ten minutes, report a "negligibly small" decrease in size with an upper limit of 0.2% for $1\text{ }\mu\text{m}$ spheres and 0.1% for smaller ones.

Five potential sources of significant systematic error are apparent in the reports of electron microscope measurements of latex spheres drawn from liquid suspension as described above. First, there is the change in particle diameter due to drying in air and subsequent evacuation. Second, there is the decrease in particle diameter due to loss of mass due to irradiation by high energy electrons. Third, there is the increase in particle diameter

due to deposition of contamination by the electron beam. Fourth, there is the determination of the point-to-point magnification of the electron image. And finally, there is the matter of properly measuring the image corresponding to that determined by geometrical-optics. Each of these potential sources of error would need to be investigated and managed in order to obtain definitive measurements from the technique.

3.B.2. Light-Scattering

As a candidate technique for direct measurement of particle sizes, especially highly spherical monosize particles in liquid or aerosol suspension, light-scattering in one or more of its many forms has conspicuous advantages. For example, it can measure such particles in their own environment, can average instantaneously over a great number of particles, and via a well-developed theory, can yield dimensional information without requiring comparison to particles of known size. Light-scattering, however, is not one thing. Rather, in contrast to the technique of electron microscope measurements of particle size, light-scattering measurements encompass a wide array of seemingly unrelated techniques and a complex of theoretical-analytical models. This report will only touch on some of the instruments and theoretical treatments in order to provide some context for the intercomparison of results and a discussion of the potential calibration techniques.

a. Light-scattering instrument systems

A major reason for the diversity of techniques and theoretical treatments of light-scattering as applied to particle size measurement is the nature of light and the number of its properties capable of carrying dimensional information about the particle which scattered it. These properties include amplitude (or intensity or photon count), phase, frequency (or wavelength), direction of polarization, and direction of propagation. In general the technique is to deduce particle size from the dependence of one of these properties upon a second one which varies as the remaining are held fixed or ignored. Some of the major types of light-scattering techniques for particle size measurements based on this type of independent-dependent variable categorization include:

- ° intensity-vs-direction of propagation measurements (referred to as angular scattering); some variations of this classic technique and their capabilities will be discussed shortly.
- ° intensity-vs-phase type measurements, which includes laser interferometry [R1, R2]; holography with one-wavelength [H16, K9] or two-wavelength [M8] illumination in normal wide-angle or forward-scatter [S9] or with computer-synthesized holographs [T6]; and array-diffraction [F3, P2].
- ° frequency-vs-direction type measurements, which includes various Doppler shift techniques [C3].
- ° photon count-vs-time measurements, which includes various photon correlation techniques [C12, G10, H14, L13].
- ° intensity-vs-presence/absence of particles, which includes the optical extinction and turbidity techniques [D15, 18, 19, 21]; this technique involves measurement in the forward-direction with scattering as one of the attenuation mechanisms for the change in intensity, but it is distinguished from forward (or near-forward or low-angle) scattering [B12, D15, L11, S6] since the unscattered beam carries the information;
- ° intensity-vs-microscope quasi-imaging, including interference contrast microscopy [S8], dark-field microscopy [D2], and array-counting [K15, R3] techniques.

Among these various light-scattering techniques with demonstrated capabilities for measurement of particle size to uncertainties in the range 100 down to 3 nm, there are, for example, angular-intensity techniques to be discussed below, laser-Doppler techniques (with reported uncertainties of about 1% for 5-15 μm particles [eg. B17], photon-counting Rayleigh-spectrometer techniques (with reported uncertainties of 0.003 μm particles [H3a]), and, for measurements of single particles, deviation techniques [eg. C24, M1, W17]. Of

these, angular intensity scattering is most interesting since it: (1) can be applied to collections of particles in suspension; (2) is suited to dimensional measurement of highly spherical, homogenous particles in the range 1-10 μm as chosen for initial standard reference particles; (3) can be implemented and theoretically treated in a straight-forward convenient way; and (4) can also add to fundamental understanding of electromagnetic scattering phenomena.

Angular scattering, which is the classic technique of light scattering for particle size measurements involving intensity-versus-angle, is applied with various ways of extracting dimensional information from the angular intensity distribution, that is, from the scattering pattern. For example, early work on latex spheres used 90° scatter, polarization ratio, extremum location, dissymmetry ratio, and spectral transmittance to obtain dimensional information [D19]. This pre-laser work achieved agreement among mean diameters as measured by the various techniques which could often be considered to be good (each within, for example, 0.01 or 0.02 μm of an average) and was occasionally strikingly good (for examples, mean diameters of a latex by the four methods of 0.808, 0.802, 0.803, and 0.805 μm) [D19].

The technique of angular scattering has been applied continually with refinements of sources (from mercury lamps [D19] to HeNe CW lasers [G1] to wavelength-tunable dye lasers [A7]), detection, and data processing techniques [K1, K2]. Kratochvil, who has published continually over the period and maintained contact with the literature, reviewed light-scattering measurements in general in 1964 [K13] and, along with original measurements [K11, K12, K14, W6, W7, W8], has compared the results of some latex sphere diameter measurements by the variety of light-scattering techniques [K10]. Gebhart, et al. have discussed the various light-scattering instruments capable of high-resolution, direct measurement of particle size which they describe as particle-size spectrometers [G1], while Willeke and Liv discussed various light-scattering instruments which are usually limited to comparison measurements, and they describe as optical particle counters [W12]. Most of the particle counters are fixed angle, intensity-ratioing devices in which the design choice is to gain simplicity and speed by trading-off angle-scanning.

Angular-scattering measurements on standard spherical particles have been made using commercial and laboratory prototype instruments which scan various segments of the angular distribution. More or less full circle devices are referred to by Marshall, et al. [M1] and Powell, et al. [R10]. That reported by Marshall has been used to scan continuously over the angular ranges 5°-175° and 185°-355° with a 2° angular acceptance at the detector [M1], while that reported on by Powell has been used to scan over an assumedly large part of the full circle at 1° intervals with a 5° acceptance [R10]. Angular-scattering instruments which scan more-or-less the half circle are those used or described by Wyatt [W15, 16], Kerker, and Powell [R10]. In the devices of Wyatt and Kerker, which are from the same manufacturer and differ only in that the former measures electrostatically-levitated individual particles [W15, 16] while the latter measures particles in suspension, the scanning range is typically 8° to 172° with a 2° acceptance. Powell's instrument was used in a modified form to scan from 45° to 115° at 5° intervals with a 5° acceptance [R10].

For each of these five angular-scattering instruments, the size of the particle doing the scattering is determined from a comparison of the observed intensity-vs-angle distribution with a theoretical distribution calculated for a specific particle size-index of refraction combination. In essence, it is a two-parameter fit of observed-vs-calculated curves. As an example of a fast measurement and achievable results, the Gucker instrument [M1, R10] uses an ellipsoidal mirror for collecting the light-scattering by a particle at its focus and a second moving mirror to scan 360° in 20 msec; uncertainties in the measurement of the diameters of individual particles ranging from 0.3 to 11 μm in size are given as 0.5 to <1%; the resulting mean diameter for a Dow (LS-1028-E) latex is given as $D = 1.189 \mu\text{m}$ with $\sigma = 0.008 \mu\text{m}$ and an index of $m = 1.588$.

Both types of angular intensity light scattering techniques, i.e., scattering from single levitated particles and scattering from collections of particles in suspension, can yield values for the distributions of particle size about a mean diameter. In single-particle scattering methods such as in Ref. C24, particles are measured serially and a mean diameter and distribution about the mean calculated from individual measured diameters. In scattering-from-suspensions methods: (1) a mean diameter alone can be determined by

a single best-fit match between an observed angular intensity pattern and one calculated for one diameter of sphere, or (2) a mean diameter and a distribution can be determined by a fit between an observed pattern and a pattern calculated as the average of a number of individual patterns for different size spheres [see, for example, Ref. K11, K12].

Potential sources of measurement uncertainty in angular intensity light scattering determinations of particle size include the effects of

- (1) deviations from sphericity of individual particles;
- (2) deviations of the index of refractions of individual microscopic particles from the known value for the bulk material;
- (3) deviations in the wavelength of the light used from the assumed value;
- (4) errors in angle measurement;
- (5) errors in intensity measurement;
- (6) finite acceptance angles detector;
- (7) deviations from planarity of incident light;
- (8) deviations from monochromaticity of incident light; and
- (9) fundamental light and limitations of Mie theory.

Quantitative determination of the systematic effects of these factors require extensive analysis which is beyond the scope of this work. Estimates of variability in results have been made, however, by numerous authors; estimates of the magnitude of systematic effects can be made, for example, by intercomparisons of results from various laboratories, such as in Ref. R10 and in this work. By inference, it appears that systematic errors of the order of 1-3% for the 1 μ m particles can be encountered, while overall uncertainties of 1% (including observed variability with estimates of systematic errors) appear to be attainable.

b. Applicable theories of light-scattering

The interaction of light with real microscopic particles is a complex physical phenomenon which can be described mathematically only in restricted, approximate forms. As applied to particle size measurement, basic theory usually treats light which is elastically scattered from, at most, one homogenous dielectric sphere. Different theoretical models are used to quantitatively describe the behavior of the light scattered from such a spherical particle and to extract the dimensional information about the particle. The choice of models depends on the dimensions of the real particle relative to the wavelength of the light ($x = 2 \pi a / \lambda$) and on the effective index of refraction of the particle relative to the medium ($m = n_{\text{particle}} / n_{\text{medium}}$).

In the limit of very small particle diameters ($D \ll \lambda$) and the limit of very large particle diameters ($D \gg \lambda$), the relevant models treat them as geometrical objects which do not interact with the electromagnetic wave. Within each of these limits, the next order approximations, for particles nearer in dimension to λ , add phase-shifts which depend on the index of refraction. For intermediate size particles, the most accurate theory treats the complex interaction of the dielectric sphere with the electromagnetic wave which describes the light.

Various elements of the five basic models have been described by, among others, Allen [A3], Born and Wolf [B11], Chu [C12], Deirmendjian [D16], Gebhart [G1], Kerker [K7], Van de Hulst [V4], and Willeke [W12], from whom this discussion is drawn. The names associated with these various models vary according to the vagaries of history and the inclinations of workers reporting (see Kerker [K7] for a discussion).

Rayleigh-scattering applies to very small particles such as air molecules. In terms of the size parameter x and the relative index m , the approximation applies for

$$(27) \quad (m-1) \rightarrow 0$$

$$(28) \quad x = \frac{2\pi r}{\lambda} < 0.3.$$

In this approximation, the particle is treated as a point dipole with a dipole strength proportional to particle volume. From Van de Hulst [V4], the intensity I at angle θ is given by

$$(29) \quad I_{\theta} = |\alpha|^2 \frac{2\pi}{\lambda_m}^4 \frac{(1+\cos^2\theta)}{2z^4}$$

where α is the volume polarizability, z is the distance from particle to detector, and λ_m is the wavelength in the medium. For homogenous spheres:

$$(30) \quad \alpha = \frac{3(m^2-1)}{(m^2+2)} \frac{v}{4}$$

which for the condition $(m-1) \rightarrow 0$ reduces to

$$(31) \quad \alpha = 2(m-1) \frac{v}{4}.$$

Since $v \sim r^3$ and $I \sim \alpha^2$,

$$(32) \quad I_{\theta} \sim r^6(1+\cos^2\theta)$$

where the angle-dependent and angle-independent terms correspond to two polarizations. In Rayleigh scattering, the intensity distribution is symmetric about 90° .

Rayleigh-Gans (or Rayleigh-Debye or Rayleigh-Gans-Debye) scattering applies to particles somewhat larger than air molecules, such as macromolecules. In this approximation, the dipole scattering of the Rayleigh approximation is modified to take into account phase-shifts of the differential volume elements over the finite volume of the sphere. Here the constraints are relaxed somewhat and the approximation applies to either:

$$(33) \quad \text{small spheres where } D \ll \lambda$$

or a particle with an index close to that of the medium:

$$(34) \quad (m-1) \rightarrow 0,$$

while the overall constraint is maintained:

$$(35) \quad \frac{2\pi a}{\lambda} (m-1) \ll 1.$$

According to Van de Hulst [A3, V4], the intensity varies in the form:

$$(36) \quad I_{\theta} = I_0 \left[\frac{k^4 v^2 (m-1)^2}{8\pi^2 Z^2} \right] \left[\frac{3}{\mu} (\sin \mu - \mu \cos \mu) \right]^2 (1 + \cos^2 \theta)$$

where

$$(37) \quad \mu = \frac{2\pi D}{\lambda_m} \sin \frac{\theta}{2} \text{ and } k = \frac{2\pi}{\lambda_m}.$$

Here the scattering intensity is asymmetric about 90° and shows maxima and minima. At the other end of the size spectrum are large particles, where $D \gg \lambda$ is the basic diffraction scattering and its phase-shift modification.

Fraunhofer diffraction applies to particles large in comparison to the wavelength, $D \gg \lambda$, and treats the particle in the limit as a circular disc. The intensity pattern is described by the familiar Bessel function equation of the Airy pattern:

$$(38) \quad I_o \sim \frac{J_1(x \sin \theta)^2}{x \sin \theta}$$

where again $x = 2\pi a / \lambda_m$. The intensity shows maxima and minima, with the first zero of the function at $\sin \theta = 1.22 / 2a$.

Anomalous diffraction applies to particles large in comparison to the wavelength $D > \lambda$, but not at the limit of geometric diffraction. In this approximation:

$$(39) \quad x \gg 1$$

while

$$(40) \quad (m - 1) \rightarrow 0.$$

Phenomenologically, the model treats a transparent sphere as having an incident ray which passes through the sphere without reflection or refraction but has a significant phase shift because of the long path length through the sphere. The total scattered field results from the interference of the Fraunhofer-contribution and the forward-scattered phase-delayed contribution.

Resonant scattering occurs when the incident electromagnetic wave physically interacts with the material of the scatterer in such a way so as to produce in the scattering properties maxima and minima which cannot be accounted for by diffraction and interference phenomena alone. The current theory best suited to handle this situation is one variously described as Mie [V4], Lorentz-Mie [R10], or Debye [K7].

Mie theory treats plane electromagnetic waves incident on and scattered from homogeneous dielectric spheres described by a size parameter $x = 2\pi a / \lambda$ and a complex index of refraction m . Scattered fields are determined from solutions of Maxwell's equations with boundary conditions consisting of continuity of field vector components at mathematical discontinuous boundaries [K7]. The resulting expressions for the angular intensity distributions for the two polarizations are:

$$(41) \quad i_1(x, m, \theta) \quad i_2(x, m, \theta)$$

These are infinite series whose terms are functions of spherical Bessel and Le Gendre polynomials. The response R of a light-scattering instrument in terms of i_1 , i_2 , $f_s(\lambda)$ (the source spectral emission function), $f_d(\lambda)$ (the detector spectral sensitivity function), $f_g(\theta, \phi)$ (the source-particle-detector geometry function), and k (a scale factor) is:

$$(42) \quad R(m, x, \theta, \phi, \lambda) = k f_s(\lambda) f_d(\lambda) f_g(\theta, \phi) \times (i_1(m, \theta, x) + i_2(m, \theta, x)).$$

While classic texts such as those by Born and Wolf [B11], Kerker [K7], and Van de Hulst [V4] show the behavior of scattering functions from Mie theory calculations for many values of the parameters m , θ , λ , and x , particle size measurements based on such calculations have serious practical limitations. First, they apply only to spheres; second, they apply solely to collections of identical spheres; third, they predict angular intensity from known index and size parameters, not vice versa; and finally, they require extensive computer calculations to numerically evaluate the series.

As a result of this latter condition, particle-size determination via Mie theory has been done in a number of ways: the most common being manual-visual matching, with interpolation, of experimentally-measured intensity curves against theoretical curves such as those in textbooks [V4] or instrument-manufacturers catalogue of curves [W5]: similar matching against individually calculated curves with best-guess input values of m and x : and computer best-fit determinations [R10].

In the evaluation of the results of the particle size determination via the Mie calculations, a number of factors have been pointed out and examined as sources of systematic error. An important source is the effect of particle non-sphericity and this subject has been extensively treated theoretically and experimentally for the cases of ellipsoids, oblate and prolate spheroids [A6, L3, L5, L7, C14, C16, W16]. The effect of a finite width of size distribution [W5] and the assumed shape of the distribution [W3, C11] has been examined, while an effect of finite detector acceptance angle has been calculated and compared using experimental results [R10].

3.B.3. Automatic Counting (and Sizing) of Particles.

a. Particle counters

The capabilities of automatic liquid-borne particle counters for providing fast, explicit histogram measurements of particle sizes over ranges of about $5 \mu\text{m}$ up to $100 \mu\text{m}$ makes them attractive as candidates for comparison calibrations of standard particles such as latex spheres and glass microbeads. Both types, optical and electrical-resistance, have comparable basic capabilities although they differ significantly in specifics. Commercially available instruments are described by Allen [A3], Davies [D8] and Willeke [W10].

Electrical-sensing-zone (or electrical resistance) particle size instruments, based on the original device by Coulter [C25], measure an effective particle volume in terms of a change in resistivity of an electrolyte from which some fraction is displaced by the particle. In a first-order model [A3], the change in resistance due to the presence of a particle in the orifice of the device can be expressed in terms of the resistivities of the electrolyte fluid ρ_e and the particle ρ_p , the cross-sectional areas of the aperture A_a and the particle A_p , and the effective fraction of the particle dimension e subtended by the aperture. This change in resistance is given by [A3]:

$$(43) \quad \Delta R = \frac{\rho_e A_p}{A} \left(1 - \frac{\rho_e}{\rho_p} \right) \frac{1}{\{1 - (1 - \rho_e/\rho_p) A_p/A_s\}}.$$

According to Allen, terms ρ_e/ρ_p can be neglected since, in practice, the response is independent of the resistivity of the particle. The equation above then reduces to

$$(44) \quad \Delta R \cong \left(\frac{\rho}{A_a^2} \right) \times (A_p \delta l) \times \left(1 - \frac{A_p}{A_a} \right)^{-1}$$

or

$$(45) \quad R \sim (\text{particle volume}) \times \left(1 - \left(\frac{A_p}{A_a} \right)^{-1} \right).$$

The magnitude of the deviation from a straight volume proportionality is shape- and size-dependent, causing a 6% effect for rod-shaped particles as well as a 5.5% error for large spherical particles ($D_p \geq 0.4 D$ aperture) [A3].

Characteristic precisions, attributed to such instruments by their manufacturers and evidenced by round-robin intercomparison [ASTM Circular C690], include repeatabilities of +1% (at 95% confidence, for all size levels) and reproducibilities of +3%. As mentioned earlier, the literature on the technique, its systematic effects, and error sources is extensive, with Allen's treatment [A3], the manufacturer's technical literature including the Coulter, Inc. bibliography, and other sources [S10, D8-13], providing input.

Optical particle counters vary in the way they measure particle dimensions, although many are characterized as measuring some projected area [G1, D8]. Using more than fifty literature citations, Willeke and Liu [W12] identify laboratory prototype and commercial devices, discuss them in terms of the effects of angular geometries, theoretical response calculations, calibration techniques, sampling efficiency, particle shape and refractive index, counting accuracy, coincidences, pulse processing, and size resolution.

In general the response R of most optical counters can be described formally as an integral over the instrument geometry, its spectral response f_s and the Mie scattering functions and their variables as described in Section 3.B.2.b. such that:

$$(46) \quad R(m, x) = \iiint [k f_s(\lambda) f_g(\theta, \phi) \times (i_1(m, \theta, x) + i_2(m, j, x))] d\theta d\phi d\lambda.$$

Resulting theoretical response functions for specific optical counters are given in graphs, discussed, or cited in the literature by Willeke [W12]. Two instruments described by Gebhart [G1] are relatively representative of the basic capabilities. One instrument, designed for particles small compared to the wavelength of light, uses a laser source and near-forward collection described as giving a volume-equivalent size independent of shape but dependent of the index of refraction in a scaling-factor type behavior; the second instrument, for particles large in comparison to wavelength, uses a white light source and low-angle collection described as giving a projected area size independent of both shape and index of refraction. A major reason for using white light is to average out the theory-based oscillations in instrument response to monochromatic light which can give apparently multivalued particle size [G1, B12]. The laser instrument is described as being able to measure particles over the size range $0.05 \mu\text{m}$ to $0.7 \mu\text{m}$ with an uncertainty of 2%; the white light instrument's range is given as 0.7 to $6 \mu\text{m}$ [G1]. A new addition to the field is a commercial optical aerosol size instrument which masks and measures segments of the Fraunhofer diffraction pattern to obtain second, third and fourth power of radius dependence [W18].

Some of the more apparent potential sources of systematic error in flow-through particle counters as reported in the literature are common to both optical and electrical-sensing types. Among these are errors in accurately counting and characterizing the whole particle

population distribution due to, for example, more than one particle in the sensing zone (coincidence), electronic noise, preferential sampling of sizes, non-discrimination of debris or agglomeration, finite-width size-interval channels, and a fine size lower detection limit.

Other potential sources of systematic error in flow-through counters are specific to the type. Among those for electrical sensing instruments, for example, are finite size of particle relative to aperture dimensions and pulse-shape dependence on wall-proximity effects. Potential error sources specific to optical counters are possible non-unique response as a function of particle size and unaccounted for dependence on particle shape or index of refraction. In comparisons of measurements by the two devices, there is the difference in volume-versus-area (or other power of radius) dependence. Some of the more apparent sources of systematic error are reported in the literature.

b. Image analyzers

Image analyzers, as adjuncts to optical or electron microscopes, can provide some degree of automatic counting and sizing of the magnified images from the microscopes. Like flow-through particle counters, they allow explicit histograms of particle size distributions to be derived from counts of individual particles of measured sizes. There are two major types of image analyzers, and they are distinguished by their basic method of measuring image size and the degree of automation in the process; in the first type of image analyzer, operator judgment is the basis of size measurement, while in the other type, the decision is machine-made.

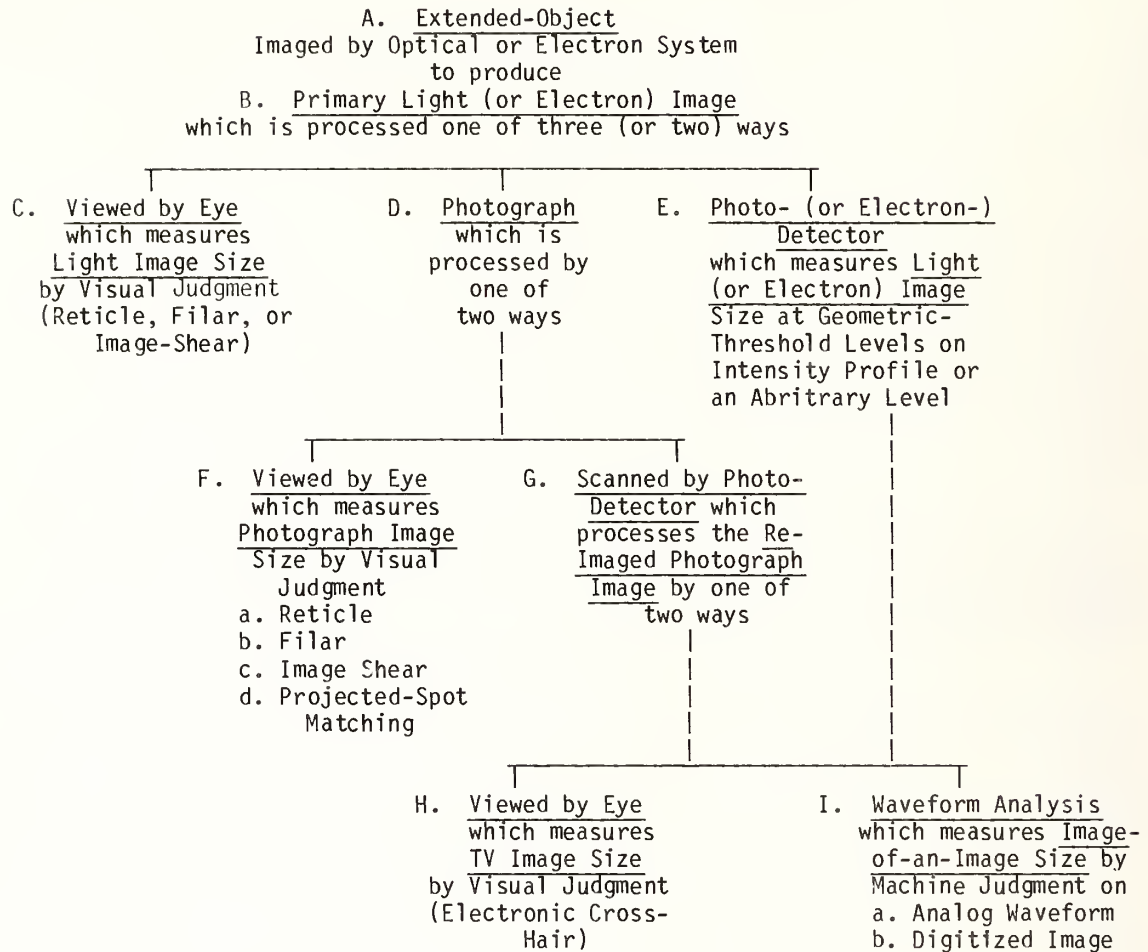
Projected-spot image analyzers are machine-assist devices which project a variable-size light spot onto a photographic print or negative and record the aperture size corresponding to the one which the operator decides gives the best fit between the size of the projected spot and the photographic image of the particle. The device is a conventional means of semi-automatically sizing and counting images of particles on TEM plates or optical microscope photos and has been applied to the sizing of latex spheres [A5, B3, C3, D3].

The second type of image analyzer is a machine-decision device and includes both digital computer-based and analog circuitry-based image processing. For either one, there are two types according to whether the image produced by the microscope is measured directly or whether the image is photographed and the photographic image is measured. Image analyzers of each type are available commercially, and their application to particle size measurement has been discussed in the literature [A3, D11-14, S10].

The relationship of image analyzers of various types to each other and to other ways of measuring the size of microscope images of particles is shown in Figure 2. Starting with particle, (A), as an object, the figure shows that the image, (B), produced by the electron or optical microscope can be processed one of three ways. In an optical microscope, the image can be viewed (C) by eye directly and the size of the light image measured with a visual eyepiece such as a reticle, a movable cross-hair filar, or an image-splitting (shearing) device. It is also possible to photograph the light image (D) and scan it by a photodetector (E). In an electron microscope, the electron beam image can be recorded directly onto a photographic plate, as in a TEM, collected to produce an image on a CRT which is in turn photographed (D), or collected for electronic processing (E).

Whether the images are recordings of the light in an optical microscope, the electrons in a TEM, or the light from the CRT screen of an SEM, photomicrographs (D) can be analyzed in one of two ways. They can be viewed (F) under low-power optical magnification and measured as in (C), a project-spot can be matched to the image size as discussed previously, or the photographs can be reimaged and scanned with a photodetector (G). A vidicon as a detector can be used to produce a TV image which has a movable electronic-crosshair for visual settings (H), or a vidicon, together with an apertured photomultiplier, a diode array, or other photodetector can be used to generate digitized or analog waveforms for a machine-based judgment of image size (I). This process, which eliminates the operator's subjective judgment of image size, can be applied directly to the original microscope image (as opposed to the photographed image), as in E to I.

Figure 2. Alternative Ways of Mesuring the Size of an Image



Systematic errors related to different edge-location criteria and related effects were discussed earlier, and image-analyzers are also susceptible. Since the effects depend on the relation of the edge-region to the image as a whole, they can be relatively independent of the microscope magnification and are observed over a range of particle sizes. For 3 μm latexes, the manufacturer reports that TEM measurements using a projected-spot analyzer differ by about 0.5 μm or about 20% from those obtained using a reticle directly on the TEM plates [B3]. For 0.25 μm latexes, another manufacturer's laboratory reports difference up to 0.05 μm or about 20% for the same two techniques [D3], depending on the size and polarity (clear spot on opaque background or vice versa) of the images processed by the analyzer. Similar systematic differences among filar, image-shearing, and TV-microscope systems, as well as a discussion of polarity-dependence, have been reported for the related case of planar objects, where differences on the order of 0.25 μm for measurements directly on the light images of 1, 3, and 10 μm objects were observed [S11, S12].

Two methods of overcoming the arbitrariness of such systematic differences have been reported. For TEM measurements on the 0.25 μm latexes, the reticle measurements were reported as producing the best agreement between the TEM results and those from other unspecified methods [D3]. For optical microscope measurements on clear and opaque planar objects, no one optical method other than photometric scanning using, for example, a theoretically-predicted threshold on the image for object-size determination, was found acceptable and free from large systematic error [N5, S11].

o o o

This brief examination of automatic particle counting techniques, especially those of flow-through counters, follows a similar examination of light-scattering and electron microscopy techniques. Each has strengths and weaknesses which complement the other two. Taken together, the three provide an attractive scheme for primary and secondary calibration of microscopic particle size reference materials, especially standard spherical particles such as polymer and glass microspheres.

Electron microscopy with its unambiguous, high-resolution, high depth of focus imaging, can yield precise and potentially accurate dimensional measurements on individual particles, in vacuo, and explicitly differentiates among particles of different shapes and morphological composition. Light-scattering can determine mean size of narrow-distribution spherical particles in their original liquid environment, averaging over many particles more or less instantaneously. Flow-through counters can provide histograms of distributions as verification of the validity of the assumptions made in light-scattering as well as rapid comparison calibrations of particles of unknown size against particles of known size as determined by electron microscopy and light-scattering taken together.

With this potential complementary relationship of electron microscopy, light-scattering, and flow-through counting as a back-drop, Part 4 of this report presents reported intercomparison measurements by these techniques on polymer spheres. As was noted in the introduction to this report, in order to best understand the behavior of a measurement technique itself, the object-to-be-measured should be as simple and lacking ambiguity as possible. Polymer spheres are in general highly spherical and therefore susceptible to dimensional characterization by a single number, the diameter; further, the distribution of sizes in a population can be very narrow (1%); and the spheres are assumedly dimensionally stable under a variety of handling conditions and over time. Further, the latex spheres marketed by Dow [B2, B3] over a period of two and nearly three decades have been measured using the same basic technique and even the same people [B16, R10]. This history has provided a metrological baseline for detailed comparisons of measurements over a range of particle sizes from $<0.1 \mu\text{m}$, most often to 1 μm , but ranging up to as much as 100 μm . This next section looks at the results of measurements on these materials, specifically the mean particle size of a number of Dow latexes as determined by different techniques. From these data, conclusions are drawn about the techniques and the materials themselves, and these conclusions are summarized in the fifth and final section of the body of this report.

4. INTERCOMPARISON OF MEASUREMENTS

This section of the report summarizes and discusses results of particle-size measurements by a number of techniques on polymer spheres, primarily Dow latex spheres, over a range of sizes from 0.08 μm to 3 μm or more. In most cases, the results are given in tables of mean diameter measured by one technique versus mean diameter measured by a second technique. The second technique is usually that of electron microscopy and is performed by the manufacturer of the polymers. Also given in most tables are the incremental- and percent fractional-differences between the apparent diameters measured by the different techniques. In order of presentation, the tabular data deal first with an overview-comparison of results for six latexes which span the range of sizes, then with flow-through counter results, followed by light-scattering results, and finally with electron microscopy measurements.

A. Comparisons of Latex Particle Measurements.

4.A.1 Specific Results Compared

Polymer spheres, especially Dow latexes, have been measured independently by various techniques and workers. They have especially desirable properties, which include a high order of sphericity, narrow size distribution, and, in many cases, a nominal size measured by the manufacturer, quoted, and assumedly accurate to hundredths or even thousandths of a micrometer (the implied accuracies are in range 0.01 to 0.001 μm) [B16].

In order to provide some estimate of the scatter among results by different techniques, Tables 6 through 11 show redrafted published compilations of mean diameters of six Dow latexes as measured by various techniques. The measurement methods include those of electron microscopy, light scattering of a number of types, and other specific techniques as indicated. Inspection of the individual tables indicates a relatively wide variation among reported values. As a basis for comparison without selecting or excluding values, the following table gives (in rounded-off numbers) the average of the values in each table, the number which constitutes the average, the RMS (root-mean-square) average deviation in μm and percent, and the range of values in μm and percent.

Mean Value (μm)	Number in Average	Average Deviation		Range of Values	
		(μm)	(%)	(μm)	(%)
3.02	12	0.048	1.6	0.08	2.6
2.70	5	0.013	0.5	0.03	1.1
1.18	16	0.058	4.9	0.26	22
0.80	9	0.033	4.1	0.09	11
0.025	16	0.008	3.2	0.026	10
0.078	6	0.005	6.4	0.014	18

Some general observations about the data in Tables 6-11 can be made based on the summary table, above. First, for the four latexes with mean diameters of less than 1.2 μm , the average deviation (which describes the spread of the results from the various techniques) is on the order of 5% and the range is on the order of 15%; as for random variations, the range of ten measurements here is about three times the average deviation [Appendix F]. Second, while there are large variations from the behavior for the smallest and largest latexes, the average deviation is very comparable to the standard deviation of the particle distributions for the latexes (as determined by electron microscopy measurements of the manufacturer, see p. 7 of the report). Third, a cursory inspection shows no readily apparent systematic relationships as, for example, between the electron microscopy and light scattering values. Finally, the data alone does not suggest which if any method is more definitive.

Table 12 shows a compilation of some other latexes for which one or more measurements besides the manufacturer's have been reported. Again, no readily apparent systematic behavior is present. Later, it will be seen that where published data has

Table 6

Diameter of Dow Latex LS-1358-38 Spheres Measured by Various Workers [Ref. K10]			
Measurement Method	Mean Diameter (μm)		
Microscopy			
Electron	2.958 ^a	3.075 ^b	3.036 ^c
Optical	(See Array)		
Angular Light Scatter			
Indiv. particles	3.011 ^e (Dry)		
Collections			
Light Scatter Other	2.96 ^f	2.975 ^f	3.02 ^d
Flow-Through			
Resistance			
Light Blockage			
Light Scatter	3.128 ^c		
Array			
Length-Count	3.00 ^b	3.02 ^f (Dry)	
Diffraction	3.03 ^b	3.04 ^f (Dry)	
Centrifuge			
Spiral			
Ultra			
Sedimentation			
Turbidity/Extinction			

a. Dow quoted Ref. K10

b. Krieger, O'Neill 1968 [Ref.K10]

c. Davidson, et al. 1967 [Ref. D6]

d. Wallace, Kratochvil [in Ref. W6]

e. Marshall, et al. 1976 [Ref.M1]

f. Robillard, Patitsas 1973 [Ref. R5]

Table 7

Diameter of Dow Latex (LS-642-6) Spheres Measured by Various Workers [Ref. R4]	
Measurement Method	Mean Diameter (μm)
Microscopy	
Electron	2.682*
Optical	(See Array Count)
Angular Light Scatter	
Indiv. particles	
Collections	2.714
	2.696
Light Scatter Other	
Flow-Through	
Resistance	
Light Blockage	
Light Scatter	
Array	
Length-Count	2.708 (Dry)
Diffraction	2.688 (Dry)
Centrifuge	
Spiral	
Ultra	
Sedimentation	
Turbidity/Extinction	

* Attributed to Dow

Table 8

Diameter of Dow Latex LS-1028-E Spheres Measured by Various Workers [Ref. R10]						
Measurement Method	Mean Diameter (μm)					
Microscopy						
Electron	1.10 ^a	1.19 ^a	1.18 ^b	1.17 ^c	1.16 ^d	1.26 ^e
Optical						
Angular Light-Scatter						
Indiv. particles	1.20 ^f	1.20 ^g	1.19 ^h			
Collections	1.20 ⁱ	1.21 ^j				
Light Scatter Other	1.20 ^j					
Flow-Through						
Resistance						
Light Blockage						
Light Scatter	1.21 ^b					
Array						
Length-Count						
Diffraction	1.20 ^k					
Centrifuge						
Spiral	1.22 ^e					
Ultra	1.00 ^l					
Sedimentation						
Turbidity/Extinction						
X-Ray Scatter						

- | | |
|-------------------------------------|--|
| a. Bradford 1979 [Ref.R10] | g. Gucker, et al. 1973 [Ref.R10] |
| b. Davidson, et al. 1967 [Ref. D6] | h. Marshall, et al. [in Ref.M1] |
| c. Porstendorfer 1971 [Ref.R10] | i. Wims, Meyer 1972 [Ref.R10] |
| d. Heard, et al. 1970 [Ref. H4] | j. Rowell, et al. [Ref.R10] |
| e. Stober, Flaschart 1971 [Ref.R10] | k. Bierhuizen, Ferron 1975 [Ref.R10] |
| f. Phillips, et al. 1970 [Ref.R10] | l. Van den Hul., Vanderhoff 1971 [Ref.R10] |

Table 9

Diameter of Dow Latex 449E Spheres
Measured by Various Workers [Ref. C23]

Measurement Method	Mean Diameter (μm)			
Microscopy	0.796 ^a	0.777 ^b	0.765 ^c	0.850 ^d
Electron				
Optical				
Angular Light Scatter				
Indiv. particles	0.784 ^e	0.764 ^e		
Collections	0.797 ^e	0.773 ^f		
Light Scatter Other				
Flow-Through				
Resistance				
Light Blockage				
Light Scatter	0.849 ^c			
Array				
Length-Count				
Diffraction				
Centrifuge				
Spiral				
Ultra				
Sedimentation				
Turbidity/Extinction				
X-Ray Scatter				

a. Attributed to Dow
b. Robbins, Jizmagian 1966
c. Davidson, et al. 1967
d. Cooper, Parfitt 1968

e. Cooke, Kerker 1973
f. Kratochvil, Wallace 1973

Table 10

Diameter of Dow Latex LS-057-A Spheres Measured by Various Workers [Ref. K10]				
Measurement Method	Mean Diameter (μm)			
Microscopy				
Electron	0.264 ^a	0.262 ^b	0.262 ^c	0.245 ^d
Optical				
Angular Light Scatter				
Indiv. particles				
Collections	0.242 ^e	0.245 ^f	0.245 ^g	0.25 ^h
Light Scatter Other				
Flow-Through				
Resistance				
Light Blockage				
Light Scatter	0.238 ⁱ	0.244 ⁱ		
Array				
Length-Count				
Diffraction				
Random Diffraction				
Centrifuge				
Spiral				
Ultra				
Sedimentation	0.248 ^j			
Turbidity/Extinction	0.245 - 0.259 ^k	0.249 ^l		
X-Ray Scatter	0.254 ^m	0.248 ⁿ		
a. Bradford 1955 [Ref.B16] b. Dobbins 1966 [Ref.D20] c. Davidson, et al. 1967 [Ref. D6] d. Davidson, Haller 1974 [Ref. D3] e. Kratochvil, Wallace 1970 [Ref.K12] f. Querfeld, et al. 1972 [Ref.K10] g. Dezelic, Kratochvil 1961 [Ref. D19]				
h. Jennings, Plummer 1968 [Ref.K10] i. Davidson, et al. 1971 [Ref.D5] j. McCormick 1964 [Ref.K10] k. Bateman, et al. 1963 [Ref.K10] l. Dezelic, et al. 1963 [Ref.D18] m. Bonse, Hart 1966 [Ref.K10] n. Brady, Gravatt 1971 [Ref. K10]				

Table 11

Diameter of Dow Latex LS-040-A Spheres
Measured by Various Workers [Ref. D3]

Measurement Method	Mean Diameter (μm)	
Microscopy		
Electron	0.088 ^a	0.078 ^b
Optical		
Angular Light Scatter		
Indiv. particles		
Collection	0.076 ^c	
Light Scatter Other		
Flow-Through		
Resistance		
Light Blockage		
Light Scatter	0.074 ^d	
Array		
Length-Count		
Diffraction		
Centrifuge		
Spiral		
Ultra		
Sedimentation	0.074 ^e	
Turbidity/Extinction		
X-Ray Scatter	0.078 ^f	

a. Bradford 1955 [Ref.B16]

b. Davidson, Haller 1974 [Ref. D3]

c. Kratochvil, et al. [in Ref. D3]

d. Davidson, Collins 1972 [in Ref. D4]

e. McCormick 1964 [in Ref. D3]

f. Bonse, Hart 1966 [in Ref. D3]

allowed comparisons of the same individual techniques over a series of latexes of different sizes, systematic differences are manifest. In the next three sections, illustrative comparisons are made for resistive-counters, light-scattering, and electron microscopy.

a. Resistive Counter Measurements

Most flow-through particle counters are comparators which can provide precise measurement of particles of unknown size relative to particles of known size against which the instruments are calibrated. Tables 13-18 show reported results for measurements made on polymer spheres with flow-through counters or calibrated against other such spheres. These tables are included here as a sampling of the levels of agreement that have been observed and reported for such measurements.

Tables 13-16 are extracted from one study involving polymer spheres from three suppliers, two different resistive-type counters, and a special electron microscopy technique [A5]. (As noted earlier, the special technique involves measurement of the shadow, through an opening in a metal film, cast by a particle as a result of metal vapor deposition [C9, C20, D5]). Over the range 0.8 μm to 11.5 μm of the six latexes in Table 13, the resistive counter measurements agree with the special electron-microscopy measurements to within +5% or so, with an arithmetic average deviation of +0.25% and an RMS average deviation of 4.3%. Some hint of systematic effects appear in the correlation of the error sign with latex source for two of the three cases; these apparent incremental differences also appear in Table 14 for two other latexes. Over the same range, 0.8 μm to 11.5 μm of latexes, in Table 15, a second resistive counter's measurements agree with the special electron microscopy measurements within 5% or so, with an arithmetic average difference of -1.2% and an RMS average deviation of 3%.

Direct comparison of the two counters for four latexes over the 0.8 μm to 11.5 μm range in Table 16, shows agreement within 5% or so, with an arithmetic average deviation of 0.25% and an RMS deviation of 3.2%. Differences this large exceed the precision reported to be characteristic of the devices themselves. For comparisons of the same types of counters, repeatabilities of 1% (95% confidence) and reproducibilities of 3% (95% confidence) are reported (ASTM circular C90), such agreement being consistent with results in Table 17 for one company's comparison of instruments at sites in three countries. For the 6.6 μm latex shown, the three instruments produced results which agree with an RMS deviation of 0.9% on median size. (They also agree with an RMS deviation of 2% on the size distribution index D_{84}/D_{50} , which is the ratio of the size greater than that of 84% of the population to the size greater than 50%).

b. Optical Microscope Measurements

In tables 18-23, measurements on polymer spheres made by three different optical microscope techniques are compared with other methods. In Table 18, the comparison is for some large (10 μm to 20 μm) DVB latexes and is between flow-through counter measurements and optical microscope/projected-spot analyzer measurements [A5]. Here the difference is clearly systematic, with the optical microscope measurements always exceeding the counter measurements by 2 to 11%, corresponding to 0.3 μm to 2.5 μm .

Table 19 shows results for nominally 5, 10, and 20 μm DVB latexes using visual image-splitting optical microscopy, visual array-counting optical microscopy, and scaled-photography scanning electron microscopy [S5]. With observed variations on the order of 0.2 μm for both the visual eyepiece and SEM measurements and 0.5 μm for the array count, the 0% to 6.5% differences between entries is on the order of the combined uncertainties and is apparently non-systematic.

While the optical microscope-vs-electron microscope comparison for large spheres in Table 19 shows some level of agreement, a more detailed and precise comparison for small spheres [C8, C9] given in Table 20 shows large systematic disagreement. Table 19, which applies to wide-distribution DVB latexes from 5 to 20 μm in size, shows optical microscope measurements (with an image-splitting eyepiece) within +0.3 μm of some (scaled photograph) SEM measurements. Table 20, which applies to narrow-distribution PS latexes from 0.5 to 3.5 μm in size, shows (using a filar eyepiece) optical microscope measurements differing

Table 12

Mean Particle Size of Ten Dow Latexes by Various Methods					
Latex Designation	Value Attributed to Dow EM	Value By Various Scattering Related Techniques			
LS-1132-B	0.091	0.085 ^a (0.094 ^R)* ^b			
LS-055-A	0.188	0.171 ^{Fc}	0.175 ^{Ld}		
LS-1047-A	0.234	0.210 ^{Xe}			
LS-1010-E	0.357	0.343 ^{Ra}			
LS-06-A	0.365	0.339 ^{Lf}	0.342 ^{Hg}		
LS-15N-8	0.511	0.503 ^{Lh}	0.515 ^{Hg}		
LS-06-A	0.557	0.537 ^{Lh}	0.594 ^{Fc}	0.561 ^{Hg}	
LS-	0.822	0.82 ^{Ai}	0.80 ^{Zi}		
LS-113-B	1.011	1.04 ^{Ai}	1.02 ^{Zi}		
LS-067-A	1.171	1.120 ^{Lh}	1.136 ^{Lj}	1.146 ^{Lk}	1.160 ^{Lg}
LS-464-E	1.305	1.276 ^{Lh}	1.242 ^{Fc}		
R: Rayleigh linewidth		H: Higher-order-Tyndall			
F: Flow microscopy		Z: Various settling			
L: Angular light scatter		A: Array			
X: X-Ray scatter		*: Ambiguous value			
a. Lee, et al. 1972 [Ref.L13].		f. Davidson, Haller 1974 [Ref. D3].			
b. Gulari, et al. 1979 [Ref.G10].		g. Pierce, Maron 1964 [Ref. P4].			
c. Davidson, et al. 1967 [Ref. D6].		h. Wallace, Kratochvil 1972 [Ref. W3].			
d. Dezelic, et al. 1963 [Ref.D18].		i. Ferron 1975 [Ref. F3].			
e. Hachisu, S. 1976 [Ref. H2].		j. Rowell, et al. 1967 [Ref.R10].			

Table 13

Mean Particle Size of Some Standard Polymer Spheres by Shadowed TEM and Coulter Counter [Ref. A5]				
Latex Source	Shadowed TEM Value	Coulter Counter Value	Difference	
			μm	%
Coulter	0.84	0.80	-0.04	-5.0
Coulter	1.31	1.35	+0.04	+3.0
Dow	1.81	1.90	+0.09	+5.0
Dow	3.36	3.54	+0.18	+5.4
Duke	5.10	4.89	-0.21	-4.3
Duke	11.55	11.26	-0.29	-2.5

Table 14

Mean Particle Size of Two PVC Latexes by Shadowed TEM and Coulter Counter [Ref. A5]				
Latex	Shadowed TEM Value	Coulter Counter Value	Difference	
			μm	%
PVC	0.87	0.99	+0.08	10.7
	0.98	1.09	+0.10	15.9

Table 15

Mean Particle Size of Some Standard Polymer Spheres by EM and Celloscope [Ref. A5]				
Latex Source	Shadowed TEM Value	Celloscope Value	Difference	
			μm	%
Coulter	0.84	0.82	0.02	2.5
Coulter	1.31	1.28	0.03	2.3
Coulter	3.59	3.45	-0.14	-3.9
Duke	3.63	3.45	-0.18	-5.0
Duke	5.10	5.00	-0.10	-2.0
Duke	11.55	11.45	-0.10	-0.9

Table 16

Mean Particle Size of Some Standard Polymer Spheres by Coulter Counter and Celloscope [Ref. A5]				
Latex Source	Coulter Counter	Cello- Scope	Difference	
			μm	%
Coulter	0.80	0.82	+0.02	2.5
Coulter	1.35	1.28	-0.07	-5.2
Duke	4.89	5.00	+0.11	2.2
Duke	11.26	11.45	+0.17	1.5

Table 17

Intercomparison of Coulter Counters in Round-Robin [Ref. A5] (μm)				
Location	D ₅₀	D ₈₄ /D ₅₀	D ₈₄	σ
USA	6.6	1.35	8.90	2.31
GB	6.7	1.34	8.98	2.28
GDR	6.6	1.30	8.58	1.98

Table 18

Sizes of Some DVB Latexes by Various Techniques [Ref. A5]			
Image-Analyzer Optical Microscope	Coulter Counter	Difference	
		μm	%
10.2 μm	9.9 μm	+0.3	2.9
13.4	13.1	+0.3	2.2
22.9	21.9	+1.0	4.4
22.2	19.7	+2.5	11.3

Table 19

Sizes of Some DVB Latexes by Various Techniques [Ref. S5]		
Visual-Eyepiece Optical Microscopy	Array Count	Scanning Electron Microscope
$5.1 \pm 0.2 \text{ }\mu\text{m}$	$5.1 \pm 0.5 \text{ }\mu\text{m}$	$5.2 \pm 0.2 \text{ }\mu\text{m}$
10.2 ± 0.1	10.4 ± 0.1	10.5 ± 0.1
19.7 ± 0.1	20.8 ± 0.5	19.5 ± 0.2

Table 20

Mean Particle Size of Seven Dow Latexes by Filar-Eyepiece Optical Microscope and Electron Microscope [Ref. C9]			
Latex Designation	Electron Microscope*	Optical Microscope (Filar)	Difference (μm)
LS-057-A	0.264	0.466	0.202
LS-061-A	0.365	0.576	0.211
LS-15N-8	0.511	0.824	0.313
LS-063-A	0.556	0.818	0.362
LS-066-A	0.814	1.181	0.367
LS-067-A	1.171	1.553	0.382
LS-886-43	1.83	2.7	0.340
LS-?	2.79	3.49	0.70

*Note: Presumably Dow latexes of these designations; author identifies them only as polystyrene spheres and gives the values here associated with Dow EM.

Table 21

TEM and Optical Array Values of Some PVC Latex Sizes [Ref. D7]			
TEM-Image of Shadow	Optical Array	Difference	
		μm	%
0.484	0.491	-0.007	- 1.5
0.503	0.510	-0.007	- 1.3
0.662	0.694	-0.032	- 4.8
0.868	0.991	-0.123	-14.1
0.938	0.996	-0.058	- 6.2
0.976	1.03	-0.058	- 5.5

Table 22

TEM-Measured Metal-Vapor Shadowed PVC Latex Particles [Ref. D7]			
Size of Images of Shadows	Size of Images of Particles	Difference	
		μm	%
0.198	0.166	-0.032	16.2
0.200	0.161	-0.039	19.5
0.662	0.560	-0.102	15.4
0.938	0.773	-0.165	17.6
0.976	0.816	-0.160	16.4

Table 23

Sizes of Some DVB Latexes by Various Techniques [Ref. T1]			
TEM Images of Shadows	TEM Images of Particles	Difference	
		μm	%
0.43	0.35	0.08	18.6
0.54	0.37	0.17	31.5
0.70	0.52	0.18	25.7
1.20	0.91	0.29	24.2

systematically from $+0.2$ to $+0.7\ \mu\text{m}$ from (replica-grating) TEM measurements. In this latter case, the largest portion of the systematic difference is attributable to error in the optical measurements which are due to, first, edge-location effects and, second, limiting resolution [C8, N5, S11-12]. An application of the array-counting technique to overcome these limitations is illustrated in Table 21 [D7]. Here special TEM measurements and optical array measurements on 0.5 to $1\ \mu\text{m}$ latexes agree within 0.01 to $0.1\ \mu\text{m}$ or so.

The special TEM technique of Table 21 is the vapor-shadowing one briefly described earlier. In this technique, an anticipated change in particular diameter due to shrinkage upon exposure to the electron beam is avoided by measurement of the diameter of the shadow of the particle produced by metal vapor deposition prior to electron irradiation. Table 22 shows the apparent diameters of the particles and their shadows for five PVC latexes [D7]; the shadow diameters are larger by a fairly consistent 17%. Table 23 shows similar data for four DVB latexes [T1]; again the shadow diameters are larger, this time by an average 25%. In the tables which follow, those electron microscopy (EM) measurements which use the vapor-shadow technique are indicated, and the shrinkage and compensation effects should be kept in mind when comparisons are made.

c. Various Optical Techniques versus Electron Microscopy

In the next eleven tables (24-34), the results of measurements on polymer spheres by various light-scattering-based techniques are given and, in most cases, compared with results from electron microscopy. For the majority of cases, the differences among results are sizable and, while often random-appearing, they occasionally hint at systematic behavior.

In Table 24 are results for four styrene latexes measured by EM and dark-field microscopy, a light-scattering technique using annular illumination or collection in an optical microscope—differences range from -24% to $+12\%$ with no apparent systematic behavior. In table 25, differences between disc centrifuge and TEM shadow measurements range between -10% and $+10\%$. In Table 26, results for fractional creaming [D2] are similar.

However, in Table 24, for eight of nine Dow latexes, results from the flow ultra-microscope, another type of angular scattering device, are consistently an average 8% above the TEM shadow values. A similar systematic difference which averages 9% is manifest for the light-scattering values from the higher-order Tyndall spectra (HOTS) for six PVC latexes in Table 28. (In Table 29, a few HOTS measurements on six DOW latexes do not exhibit such systematic behavior.)

Table 30 summarizes an early, pre-laser-era comparison of results from five light-scattering techniques on eleven latexes, including eight Dow latexes, and it first demonstrated probable systematic differences between results from light-scattering measurements and electron-microscopy measurements made by the latex manufacturer. The light-scattering (LS) techniques included transmittance, 90° scattering, dissymmetry ratio, polarization ratio, and location of extrema in the angular scattering patterns. Averages for the various LS techniques appear in column 8; for the eight Dow latexes, the mean LS values systematically differ from the EM values in column 2, with the EM values being greater by an average $0.016\ \mu\text{m}$.

The comprehensiveness of measurements such as those summarized in Table 30 allows comparisons and conclusions which more limited data collection do not. For example, in Table 31, the few results available for Rayleigh linewidth light-scattering measurements, based on Stokes' size-dependent velocity equations rather than Mie-type scattering equations, do not show consistent behavior. Enough internal consistency among various light-scattering results does exist, however, to make averages over various LS techniques legitimate. The degree of consistency is shown in Tables 32-34 for individual latexes.

Table 32 shows the mean values at 95% confidence limits of the particle size of a nominally $0.25\ \mu\text{m}$ Dow latex using various light scattering techniques. The mean of the twelve entries for various techniques (Table 10) is $0.247 \pm 0.005\ \mu\text{m}$, a value which overlaps all but the flow ultramicroscopy values. Table 33 shows similar results for a nominal $1.2\ \mu\text{m}$ latex, with the average of seven mean LS values being $1.196 \pm 0.009\ \mu\text{m}$. Table 34 for nominal $3\ \mu\text{m}$ spheres, which have size distributions about 10% of nominal (Figure 1),

Table 24

Mean Particle Size of Some Styrene Latexes by
Electron and Dark-Field Optical Microscopy [Ref. D2]

Styrene Latex	Electron Microscopy	Dark Field Optical M.	Difference	
			μm	%
S39	0.213	0.265	-0.052	-24.4
S39	0.126	0.140	-0.014	-11.1
S37	0.091	0.078	+0.013	+14.2
S36	0.074	0.065	+0.009	+12.2

Table 25

TEM and Disc Centrifuge Value of Some PVC Latex Sizes [D7]			
TEM Image of Shadow	Disc Centrifuge	Difference	
		μm	%
0.0525	0.0471	0.0054	10.3
0.0822	0.0780	0.0042	5.1
0.200	0.215	-0.015	- 7.5
0.285	0.289	-0.004	- 1.4
0.484	0.543	-0.059	-12.2
0.503	0.552	-0.049	- 9.7

Table 26

TEM and Fractional Creaming Values of Some PVC Latex Sizes [Ref. D7]			
TEM Shadow of Image	Fractional Creaming	Difference	
		μm	%
0.0525	0.0490	0.0035	6.7
0.0822	0.0840	-0.0018	- 2.2
0.200	0.195	0.005	2.5
0.662	0.770	-0.108	-16.3

Table 27

Mean Particle Size of Some Dow Latexes by TEM and Light-Scatter Technique [Ref. D5,D6]				
Latex Designation	TEM-Image of Shadow	Flow-Ultra- Microscope	Difference	
			μm	%
LS-055-A	0.177	0.171	0.006	3.4
LS-057-A	0.262	0.280	-0.018	- 6.9
LS-061-A	0.350	0.365	-0.015	- 4.3
LS-063-A	0.510	0.594	-0.084	-16.5
LS-449-E	0.765	0.849	-0.084	-11.0
LS-464-E	1.087	1.242	-0.155	-14.3
LS-1028-E	1.183	1.213	-0.030	- 2.5
L6064-36	2.024	2.211	-0.187	- 9.2
EP-1358-36	3.036	3.128	-0.092	- 3.0

Table 28

TEM and Higher-Order Tyndall Spectra
Values of Some PVC Latex Sizes [Ref. D7]

TEM-Image of Shadow	Higher Order T-Spectra	Difference	
		μm	%
0.285	0.326	-0.041	-14.4
0.484	0.512	-0.028	- 5.8
0.503	0.548	-0.045	- 8.9
0.662	0.720	-0.058	- 8.8
0.868	0.953	-0.085	- 8.9
0.976	1.04	-0.064	- 6.6

Table 29

Mean Particle Diameter of Six Dow Latexes by Higher-Order-Tyndall Spectra [Ref. P4]				
Latex Designation	Value Attributed to Dow EM	HOTS* Value	Difference μm	%
LS15N-7	0.340	0.329	-0.011	-3.2
LS-061-A	0.365	0.342	-0.023	-6.3
LS-15N-8	0.511	0.515	+0.004	7.8
LS-063-A	0.557	0.561	+0.004	7.2
LS-066-A	0.814	0.799	-0.015	-1.8
LS-067-A	1.171	1.160	-0.011	0.9

*Entries are single value or average of two which differ from 0.2 to 2%.

Table 30

Comparison of Mean Particle Diameter of Eleven Dow and non-Dow Latexes
by Various Light-Scattering Techniques by Same Workers* [Ref. 19]

Latex Numbers	EM Value	Light Trans	90 Scttr	Dissym Ratio	Polar Ratio	Extrm Locat	Mean LS
BASF-1**	0.037**	0.030	0.029	---	---	---	0.029
BASF-2**	0.047**	0.042	0.042	0.050	---	---	0.045
BASF-3**	0.072**	0.069	0.058	---	---	---	0.064
LS-040-A	0.088	0.076	0.073 0.074	0.078 0.080	---	0.076	0.076
LS-15N-23	0.138	0.120	0.118 0.120	0.124 0.120	---	0.118	0.120
LS-055-A	0.188	0.167	0.182 0.176	0.175	---	---	0.175
LS-057-A	0.264	0.240	0.249 0.240	0.241 0.242	0.254	0.248	0.245
LS-061-A	0.365	0.329	0.333 0.338	0.346 0.334	0.331	0.360	0.339
LS-063-A	0.557	0.522	0.526 0.537	0.552	0.534	0.531	0.534
LS-066-A	0.814	0.784	0.808 0.807	0.802 0.805	0.803	0.805 0.808	0.803
LS-067-A	1.171	1.185	1.156 1.180	1.164 1.190	1.146	1.158 1.155	1.167

* Dezelic and Kratochvil 1961 [Ref. 19]

** Non-Dow latexes; all others Dow latexes with electron microscopy by Dow.

Note: Second values at different wavelengths of mercury arc source
(col. 4,5) or different angular widths of the detector acceptance
aperture (col.7)

Table 31

Mean Particle Size of Some Dow Latexes by Rayleigh-
Linewidth Light Scatter and Electron Microscopy

Latex Designation	EM	Rayleigh Linewidth	Difference	
			μm	%
LS-1028-E	1.192 ^a	1.20 ^b	-0.01	+0.7
LS-1010-E	0.357 ^c	0.343 ^c	+0.018	-3.9
LS-1047-E	0.234	[moments only] ^d		
LS-1132-B	0.091	0.0847 ^c	+0.063	-6.9
LS-"910" ^d	0.0884 ^d	0.0942 ^d	+0.006	+6.6

a. Bradford 1979 in Ref. R10

b. Rowell, et al. 1979 [Ref. R10]

c. Lee, et al. 1972 [Ref. L13]

d. Gulari, et al. 1978 [Ref. G10]

e. Chu, et al. 1979 [Ref. C11]

Table 32

Averaged Values of Mean Particle Size of Dow Latex LS-057-A from Various Optical Techniques [Table 10]			
Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	4	0.245 μm	$\pm 0.004 \mu\text{m}$
	6	0.247	± 0.007
Flow Microscopy	2	0.241	± 0.008
Other-Light-Type**	2	0.249	± 0.001
	4	0.250	± 0.006
X-Ray Scatter	2	0.251	± 0.008
All But X-Ray	12	0.247	± 0.005

*See Appendix G for method of calculating tolerances.

**Sedimentation and turbidity entries of Table 10.

Table 33

Averaged Values of Mean Particle Size of Dow Latex LS-1028-E from Various Optical Techniques [Table 8]			
Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	7	1.196 μm	<u>+0.009</u> μm
Array Diffraction	1	1.20	
Flow Microscopy	1	1.213	
Other-Light-Type	1	1.220	

*See Appendix G for method of calculating tolerances.

Table 34

Averaged Values of Mean Particle Size of Dow Latex LS-1358-38 from Various Optical Techniques [Table 6]			
Method of Measurement	Number in Average	Average of Means	Tolerance of Average*
Angular Scatter	4	2.992 μm	$\pm 0.027 \mu\text{m}$
Array Count	2	3.010	± 0.025
Array Diffraction	2	3.035	± 0.013
Flow Microscopy	1	3.128	

*See Appendix G for method of calculating tolerances.

also shows light-scattering values agreeing within about 1% at the 95% confidence level. It is the consistency of data such as these which permits combining mean values from various light-scattering techniques to obtain an aggregate "light-scattering value" of particle diameter which may be compared, as it later will be, with an electron microscopy value. In the next eight tables (35-42), the internal consistency of electron microscopy results are examined.

d. Intercomparison of Electron Microscopy Results

Table 35 shows electron-microscope values of mean particle size for twenty-one Dow latexes as measured by Dow and various others with thirteen different workers. For latexes nominally 0.09 μm to 3.5 μm in size, the results differ from -7% to +16% and -0.08 μm to +0.22 μm . Of the thirty-six entries in Table 35, the differences between the size attributed to Dow EM and those of others is negative in only six of the thirty-six. Thus, there is a suggestion that the mean diameters as measured by Dow are systematically higher than those by other EM workers. In the next five tables, comparisons are made between results of Dow and those of four other workers for a series of latexes over a range of sizes.

Table 3 shows EM results for nine Dow latexes from Dow EM measurements and as measured by Davidson, *et al.* [D5, D6]. Except for three latexes where results are suspect because widely different distributions in sizes were observed (see Table 37), the six latexes have Dow EM values which are an average 0.021 μm greater. Table 38 shows EM results for another group of nine Dow latexes in a comparison of Dow results and those of Heard, *et al.* [H4]. Except for one of the nine latexes, the mean particle diameters attributed to measurements by Dow are greater by an average of 0.02 μm . While the measurements on six latexes by Dobbin in Table 29 show three values which are greater than Dow and three which are less, the results on four latexes by Davidson and Haller in Table 40 are less than the Dow values by an average of 0.02 μm .

The likely cause of systematic differences in the measurements of mean particle size by various electron microscopy groups lies in the edge-location aspect of dimensional measurements by imaging techniques as discussed earlier. The effect of choosing, explicitly or implicitly, a different relative intensity level on an image intensity profile is shown in Tables 41 and 42. Table 41 shows that the apparent size of a nominal 0.25 μm particle imaged with a TEM varies by up to 20% depending on the method used to measure the size of the image on the plate: with a filar eyepiece or an image analyzer, and whether directly on the plate, a contact print, or an enlargement photo. Analogously, Table 42 shows that the apparent size of a nominal 3 μm particle imaged with a TEM varies by up to 30% depending on whether a reticle eyepiece or projected-spot analyzer is used to measure the size of the image. With these potential effects as background, the final five tables (43-47) show comparisons between various light-scattering and electron microscopy results for a number of Dow latexes.

4.A.2. Generalizations from Comparisons

Table 43 is a compilation of electron microscopy and light-scattering results for twenty-five Dow latexes covering a range of sizes from nominally 0.09 μm to 3.5 μm . In columns 2 through 4 are given mean particle diameters for the latexes as attributed to Dow's electron microscopy measurements as an average electron microscopy measurements by other groups, and as an average of various light-scattering techniques. Where averages are given, the number of means averaged, the average mean, the 95% confidence limits, and the source tables are indicated. Of the twenty-five latexes, twenty-one have two or more independent electron microscopy measurements, fifteen have light-scattering measurements, and ten have two independent electron microscopy measurements as well as light scattering measurements. In Table 43, comparison of the Dow EM and other EM entries indicates that in sixteen of the twenty-one cases, the Dow value is greater than the other.

In the next two tables, comparisons are made between the average light scattering results and the Dow and non-Dow EM results. Table 44 shows a comparison of Dow electron microscopy values and average angular light-scatter values for the mean particle diameter of twelve Dow latexes over a range of sizes from nominally 0.09 μm to 1.2 μm . In eleven of the twelve cases, the Dow EM values are greater than the light-scatter value, the average difference being 0.014 μm . Table 45 shows a comparison of non-Dow electron microscopy

Table 35

Electron-Microscope Values of Mean Particle Size
of Some Dow Latexes by Various Workers

Latex Designation	Size Attributed to Dow EM	Size By Others EM	Difference μm	%
LS-040-A ^a	0.088	0.078 ^b	0.01	11.3
LS-1132-B	0.091	0.085 ^k	0.01	6.9
LS-1044-E	0.109	0.100 ^e	0.01	8.3
LS-052-A	0.126	0.119 ^c	0.01	5.6
LS-1045-E	0.176	0.16 ^e	0.02	9.1
LS-055-A	0.188	0.177 ^d	0.01	5.9
LS-1047-E	0.234	0.22 ^e	0.01	6.0
LS-057-A ^a	0.264	0.262 ^d	0.00	0.8
	0.264	0.262 ^c	0.00	0.8
	0.264	0.245 ^b	0.02	7.2
LS-1010-E	0.357	0.343 ^l	0.01	3.9
	0.357	0.33 ^e	0.03	7.9
LS-061-A	0.365	0.33 ^e	0.04	9.6
	0.365	0.350 ^d	0.02	4.1
	0.365	0.33 ^f	0.04	9.6
	0.365	0.336 ^b	0.03	8.0
	0.365	0.368 ^c	0.00	0.8
LS-1029-E	0.500	0.50 ^e	0.00	0.0
LS-063-A ^a	0.557	0.510 ^d	0.05	8.4
	0.557	0.587 ^c	-0.03	-5.4
LS-1012-E	0.714	0.74 ^e	-0.03	-3.6
LS-449-E	0.796	0.777 ^c	0.02	2.5
	0.796	0.765 ^d	0.03	3.9
	0.796	0.850 ^j	-0.05	-6.8
	0.790	0.760 ^b	0.03	3.8
LS-1114-B	0.813	0.76 ^e	0.05	6.5
LS-1028-E	1.192 ⁱ	1.183 ^d	0.01	0.8
	1.192	1.17 ^m	0.02	1.8
	1.192	1.16 ^e	0.03	2.7
	1.192	1.26 ⁿ	-0.07	-5.7
LS-464-E	1.305	1.087 ^d	0.22	16.8
	1.305	1.343 ^c	-0.04	-2.9
LS-886-43	1.81	1.81 ^j	0.00	0.0
LS-6064-36	2.050	2.024 ^d	0.03	1.3
LS-1358-38	2.958	3.036 ^d	-0.08	-2.6
EP-1358-35	3.49	3.36 ^j	0.13	3.7

a. Bradford, Vanderhoff 1955 [Ref.B16]

b. Davidson, Haller 1974 [Ref. D3]

c. Dobbins 1966 [Ref.D20]

d. Davidson, et al. 1967 [Ref. D6]

e. Heard, et al. 1970 [Ref. H4]

f. Claver, Farnham 1972 [Ref.C20]

g. Cooper 1968 [in h]

h. Kerker 1973 [Ref.C23]

i. Bradford 1979 [in Ref.R10]

j. Aliet 1976 [Ref. A4]

k. Chu, et al. 1979 [Ref.C11]

l. Lee, et al. 1972 [Ref.L13]

m. Porstendorfer 1972 [in h]

n. Stober, et al. 1971 [in h]

Table 36

Electron-Microscope Values of Mean Particle Size of Some Dow latexes by Two Workers				
Latex Designation	Dow-Bradford EM [Ref. B16]	Davidson, et al. EM [Ref.D5,D6]	Difference μm %	
LS-055-A	0.1881	0.1770	0.011	5.8
LS-057-A	0.2638	0.2617	0.002	0.8
LS-061-A	0.3646	0.3499	0.015	4.0
LS-063-A	0.5567	0.5101	0.047	8.4
LS-449-E	0.7962	0.7646	0.032	4.0
LS-464-E	1.3046	1.0867	0.218	16.7
LS-1028-E	(1.0992)	(1.1827)	(-0.084)	(-7.6)
	1.199*	1.1827	0.016	1.4
L6064-36	2.049	2.0240	0.025	1.2
EP-1358-36	2.9583	3.0356	-0.077	-2.6
*Redetermination [Ref. R10]				

Table 37

Comparison of Size Distribution Standard Deviations of Some Dow Latexes by Two Workers [Ref. D5,D6]				
Latex Designation	Normal Size (μm)	Distribution (μm)		Ratio
		Dow-Bradford	Davidson, et al.	
LS-055-A	0.19	0.0076	0.0106	1.4
LS-057-A	0.26	0.006	0.0144	2.4
LS-061-A	0.37	0.0079	0.0198	2.5
LS-063-A	0.56	0.0108	0.0267	3.4
LS-449-E	0.80	0.0083	0.0624	7.5
LS-464-E	1.30	0.0158	0.2348	14.9
LS-1028-E	1.20	0.0159	0.636	40.0
L-6064-36	2.05	0.0180	0.1088	6.0
EP-1358-38	2.96	0.0150	0.1904	12.7

Table 38

Electron-Microscope Values of Mean Particle Size of Some Dow Latexes by Two Workers [Ref. H4]				
Latex Designation	Bradford-Dow EM	Heard, et al. EM	Difference μm %	
LS-1044-E	0.109	(0.103)*	(0.006)	5.5
		0.100*	0.009	8.3
LS-1045-E	0.176	0.16*	0.016	9.1
LS-1047-E	0.234	0.22*	0.014	6.0
LS-1010-E	0.357	0.33	0.027	7.6
(LS-061-A)	0.365	(0.33)*	(0.035)	(9.6)
LS-1029-E	0.500	0.50	0.00	0.0
LS-1012-E	0.714	0.74	-0.026	-3.6
LS-1114-E	0.813	0.76	0.053	6.5
LS-1028-E	(1.099)	(1.16)	(-0.061)	(-5.6)
	1.192**	1.16	0.032	2.7

*Dimensionally measured by ratio of image size with other particles;
other unstarred entries were scaled with grating replica.

**Redetermination by Dow [Ref. R10]

Table 39

Electron-Microscope Values of Mean Particle Size
of Some Dow Latexes By Two Workers [Ref. D20]

Latex Designation	Value Dow EM	Dobbins, et al. EM	Difference	
			μm	%
LS-052-A	0.126	0.119	-0.007	-5.6
LS-057-A	0.264	0.262	-0.002	-0.8
LS-061-A	0.365	0.368	+0.003	+0.8
LS-063-A	0.557	0.587	+0.030	+5.4
LS-449-E	0.796	0.777	-0.019	-2.4
LS-404-E	1.305	1.343	+0.038	+2.9

Table 40

Electron-Microscope Values of Mean Particle
Size of Some Dow Latexes by Two Workers [Ref. D2, D3]

Latex Designation	Dow-Bradford EM	Davidson, Haller EM	Difference	
			μm	%
LS-040-A	0.088	0.078	+0.01	11.4
LS-057-A	0.264	0.245	+0.02	7.2
LS-061-A	0.365	0.336	+0.03	8.0
LS-449-E	0.796	0.760	+0.04	3.8

Table 41

Dependence of Apparent Particle Size on Method of Sizing Image on TEM Plate [Ref. D3]				
Method of Sizing Image	Image Sharpness Index	Apparent Size	Relative Size Difference	
			Ratio	%
Filar Eyepiece				
Orig. negative with clear spot of 3mm diameter	1.0	0.254	1.03	+3
	0.9	0.249	1.01	+1
	0.6	0.247	1.00	
Orig. negative with opaque spot of 3mm diameter	1.0			
	0.9	0.218	0.88	-12
	0.6	0.215	0.87	-13
Contact print with clear spot of 3mm diameter	1.0	0.219, 0.202	0.89, 0.82	-11, -18
	0.9	0.222, 0.212	0.90, 0.86	-10, -14
	0.6	0.199, 0.196	0.80, 0.79	-20, -21
Image Analyzer				
Enlargement* with clear spot of 6-8 mm diameter	1.0*	0.247	1.00*	0%
	0.9	0.242	0.98	-2%
	0.6	0.220	0.89	-11%

* Method recommended by authors quoted

Table 42

Dependence of Apparent Particle Size of Four Dow Latexes on
Method of Sizing Images on TEM Plate: Reticle Eyepiece-
Versus-Automatic Projected Spot Analyzer [B3]

Reticle Eyepiece		Projected-Spot		RE/PS	Difference	
D_n	σ_n	D_n	σ_n		μm	%
2.82	0.25	3.72	0.27	1.1	-0.9	+32
3.00	0.12	3.20	0.19	1.6	-0.2	+ 7
3.08	0.21	3.55	0.23	1.1	-0.5	+15
3.14	0.28	3.61	0.24	0.9	-0.5	+15
6.4	2.0	6.8	1.9	0.9	-0.4	+ 6

Table 43

Comparison of Dow Electron Microscopy Values
with Other EM and Light-Scattering

Latex Designation	Value Dow EM	Other EM ^a		Light-Scatter	
		Number	Average	Number	Average
LS-040-A	0.088	1	0.078	6	0.076 \pm 0.002 ^b
LS-1132-B	0.091	1	0.085	1	0.085
LS-1044-E	0.109	1	0.100		
LS-15N-23	0.138			6	0.120 \pm 0.002 ^b
LS-052-A	0.126	1	0.119		
LS-1045-E	0.176	1	0.160		
LS-057-A	0.188	1	0.177	5	0.175 \pm 0.007 ^b
LS-1047-E	0.234	1	0.220		
LS-057-A	0.264	3	0.256 \pm 0.013	10	0.245 \pm 0.004 ^c
LS-1010-E	0.357	2	0.337 \pm 0.016	1	0.343
LS-061-A	0.365	5	0.335 \pm 0.008	7	0.339 \pm 0.008 ^b
LS-1029-E	0.500	1	0.50		
LS-15N-8	0.511			1	0.503
LS-063-A	0.557	2	0.549 \pm 0.096	6	0.534 \pm 0.007 ^b
LS-1012-E	0.714	1	0.74		
LS-449-E	0.796	3	0.788 \pm 0.046	4	0.780 \pm 0.014 ^d
LS-1114-E	0.813	1	0.76		
LS-066-A	0.814			8	0.803 \pm 0.006 ^b
LS-067-A	1.171			8	1.167 \pm 0.011 ^b
LS-1028-E	1.192	4	1.193 \pm 0.050	6	1.195 \pm 0.009 ^e
LS-464-E	1.305	1	1.215	1	1.276
LS-886-43	1.81	1	1.81		
LS-6064-36	2.050	1	2.024		
LS-1358-38	2.958	1	3.036	4	2.992 \pm 0.027 ^f
EP-1358-35	3.49	1	3.36		

a. Table 35
b. Table 19
c. Tables 32

d. Table 9
e. Table 33
f. Table 34

Table 44

Comparison of Dow Electron Microscopy and Average Angular Light Scatter
Values of Mean Particle Size for Twelve Dow Latexes [Table 43]

Latex Designation	Value Attributed to Dow EM	Average Value Light Scatter	Difference μm
LS-040-A	0.088	0.076	0.012
LS-1132-B	0.091	0.085	0.006
LS-15N-23	0.138	0.120	0.018
LS-055-A	0.188	0.175	0.013
LS-057-A	0.264	0.245	0.019
LS-1010-E	0.357	0.343	0.014
LS-061-A	0.365	0.339	0.026
LS-15N-8	0.511	0.503	0.008
LS-063-A	0.557	0.534	0.023
LS-449-E	0.796	0.780	0.016
LS-067-A	1.171	1.167	0.004
LS-1028-E	1.192	1.196	-0.004

Table 45

Comparison of Non-Dow Electron Microscopy and Average Light Scatter
Values of Mean Particle Size for Eight Dow Latexes [Table 43]

Latex Designation	Average of Non-Dow EM	Average Light Scatter
LS-040-A	0.078 μm	0.076 \pm 0.002 μm
LS-1132-B	0.085	0.085
LS-055-A	0.177	0.175 \pm 0.007
LS-057-A	0.256 \pm 0.013	0.245 \pm 0.004
LS-1010-A	0.337 \pm 0.016	0.343
LS-061-A	0.335 \pm 0.008	0.339 \pm 0.008
LS-063-A	0.544 \pm 0.096	0.534
LS-1012-E	0.788 \pm 0.046	0.780 \pm 0.014
LS-1028-E	1.193 \pm 0.050	1.196 \pm 0.009

values and average angular light-scatter values for nine Dow latexes over the same range of sizes as in Table 44. For these nine latexes, there is no significant difference between the light-scattering and non-Dow EM values, and in most cases, the respective values agree within the uncertainty of either value. It can be seen from Tables 44 and 45 that other non-Dow EM values are in essential agreement with LS values. As a result, a comparison was made between Dow EM values and a combined average of other EM and LS values.

Table 46 shows the comparison for twenty-four Dow latexes between the mean particle diameter as attributed to Dow electron microscopy and the average value of light-scattering and other electron microscopy values as compiled in this report. For twenty-one of the twenty-four latexes, the Dow EM value is greater than the average other-EM and LS value, and for the twenty-four latexes shown, the average difference, computed as a number (n)-weighted average, is $+0.0130 \mu\text{m}$. For the seventeen narrow-distribution particles, that is those with mean diameters of less than $1 \mu\text{m}$, the number (n)-weighted average difference is $0.0158 \mu\text{m}$. Based on this table, the conclusion drawn is that the mean particle diameters measured by the manufacturer of the latexes is systematically different from other EM and LS values by about $0.015 \mu\text{m}$ and that this difference may be a result of systematic effects in the EM values. This conclusion is in accord with the observations made by Kratochvil (as in Table 7 here) except that it is a more restricted one; for as Tables 44 and 45 indicate, EM values can be in accord with LS values, although Dow's EM values in these cases may not be.

As a note on the efficacy of vapor-shadow techniques, Table 47 shows results for six Dow latexes by TEM shadow and the average of LS and other EM. While the arithmetic average difference is $+0.0015 \mu\text{m}$, the large RMS average difference of $0.015 \mu\text{m}$ makes it impossible to conclude whether the vapor-shadow method yields results more in agreement with other techniques than the direct EM measurements on particles themselves.

Table 46

Comparison of Vapor-Shadow Diameter and Average of Light Scatter and Other EM Values			
Latex Designation	TEM Shadow Image*	Av. LS + Other EM	Difference (μm)
LS-055-A	0.177	0.175	+0.002
LS-057-A	0.262	0.248	+0.014
LS-061-A	0.350	0.337	+0.013
LS-063-A	0.510	0.538	-0.028
LS-449-E	0.765	0.783	+0.018
LS-1028E	1.183	1.193	-0.010

Table 47

Comparison of Mean Particle Size Attributed to Dow EM and Average Value from Light-Scattering and Others' Electron Microscopy [Tables 44 and 45]

Latex Designation	Value Attributed to Dow EM	Av. LS & Other EM n	Value	Difference* μm
LS- 040-A	0.088	7	0.076	0.012
LS-1132-B	0.091	2	0.085	0.006
LS-1044-E	0.109	1	0.100	0.009
LS- 052-A	0.126	1	0.119	0.007
LS- 15N-7	0.138	6	0.120	0.018
LS-1045-E	0.176	1	0.160	0.016
LS- 055-A	0.188	6	0.175	0.013
LS-1047-E	0.234	1	0.220	0.014
LS- 057-A	0.264	13	0.248	0.016
LS-1010-E	0.357	3	0.339	0.018
LS- 061-A	0.365	12	0.337	0.028
LS-1029-E	0.500	1	0.500	0.000
LS- 15N-8	0.511	1	0.503	0.008
LS- 063-A	0.557	8	0.538	0.019
LS-1012-E	0.714	1	0.74	-0.026
LS- 449-E	0.796	7	0.783	0.013
LS-1114-B	0.813	1	0.76	0.053
LS- 067-A	1.171	4	1.167	0.004
LS-1028-E	1.192	10	1.195	-0.003
LS- 464-E	1.305	2	1.246	0.059
LS-886-43	1.81	1	1.81	0.000
LS6064-36	2.050	1	2.024	0.026
LS1358-38	2.958	5	3.001	-0.043
EP1358-35	3.49	1	3.36	0.13

*Average deviation, computed from the number-n weighted differences for the 17 latexes of $D < 1 \mu\text{m}$ is + 0.0158 μm ; for the 24 latexes shown, the average is + 0.0130 μm .

5. REPORT CONCLUSIONS

The purpose of this report has been to look at those particle measurement techniques which potentially can be used as:

- (1) reference methods for definitive primary dimensional-calibration of microscopic spherical particle reference materials; and
- (2) comparison methods for convenient transfer calibrations from the reference method to bulk calibrations.

The impressive consistency of measurements of mean particle diameters of Dow polystyrene latex sphere by transmission electron microscopy in the laboratories of the latexes' manufacturer has provided a substantial basis for conclusions regarding both reference and comparison techniques.

From comparisons among EM measurements by the manufacturer, EM measurements by independent workers, and LS measurements by various groups, the following conclusions were drawn:

- Electron microscopy and light-scattering can yield mean particle diameters for narrow-distribution populations of polystyrene spheres which agree within the combined uncertainties and sometimes at the level of a few thousandths of a micrometer, i.e. nanometers.

- The electron microscopy values attributed to Dow differ systematically by an average value of approximately $0.015\text{ }\mu\text{m}$ from the average of other electron microscopy and light-scatter values.

- Electron microscopy and light-scattering measurements provide good cross-checks of each other and the two in combination can provide a definitive reference method for particle diameter calibrations.

- Flow-through particle counters can provide effective comparison transfer calibrations. The three methods complement each other, each yielding unique information. Electron microscopy can give definitive measurements of a limited number of particles; light-scattering can give an average diameter for a narrow distribution of particles in their normal liquid environment; flow-through counters can give an explicit histogram of the size distribution of the population, whenever the instrumental uncertainty is significantly less than the population distribution.

Finally, comparison of results by various techniques indicates that by means of the complementary electron microscopy - light scatter - flow-through counter approach, narrow distribution spherical polymer particles with mean diameters in the range $0.1\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$ can be calibrated with total uncertainties on the order of $\pm 0.005\text{ }\mu\text{m}$, $1\text{ }\mu\text{m}$ particles with an uncertainty of $0.01\text{ }\mu\text{m}$, and larger particles with total uncertainties on the order of the width of the total population distribution.

In conclusion, the evidence compiled in this report concerning some of the advantages, disadvantages, and relative performance characteristics of light-scattering, flow-through counting, and electron microscopy has lead to developmental work at NBS on these techniques for calibration of particle size standard reference materials.

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Appendix A

Identified Domestic Suppliers of Standard
Spherical Particles or Test Dusts

- AC Spark Plug Division
General Motors Corporation
AC Spark Plug Bldg.
Flint, MI 48556
- Coulter Electronics
590 West 20th Street
Hialeah, FL 33010
- Dow-Diagnostics Division
Dow Chemical Company
Box 68511
Indianapolis, IN 46268
- Duke Scientific Corporation
445 Sherman Avenue
Palo Alto, CA 94306
- Fluid Power Research Center
Oklahoma State University
Stillwater, OK 74074
- HIAC Division
Pacific Scientific Company
4719 West Brook Street
Montclair, CA 91763
- Microspheres Incorporated
14930 East Romona Blvd.
Baldwin Park, CA 91706
- Particle Information Service Incorporated
2957 Woodland Park Road
Grants Pass, OR 97526
- Poly Sciences
Paul Valley Industrial Park
Warrington, PA 18976
- Royco Instrument Company
141 Jefferson Drive
Menlo Park, CA 94025

Part I. Manufacturers and Addresses

Adams, L. Ltd, Minerva Road, London, NW10.
Addy Products Ltd, Solent Industrial Estate, Botley, Hampshire SO3 2FQ.
Aerograph Co., Lower Sydenham, London SW26.
Agar, Alan, W., 127 Rye Street, Bishop's Stortford, Hertfordshire.
Airflow Development, 31 Lancaster Road, High Wycombe, Buckinghamshire.
Airsupply International Gateway House, 302-8 High Street, Slough, Berkshire.
Alpine, Augsburg, W. Germany.
Ameresco Inc., 101 Park Street, Montclair, New Jersey 07042, U.S.A.
American Instruments Co., 8030 Georgia Avenue, Silver Springs, Maryland, U.S.A.
Anderson 2000 Inc., P.O. Box 20769, Atlanta, Georgia 30320, U.S.A.
Applied Research Laboratories, Wingate Road, Luton, Bedfordshire.
A.T.M. Corporation, Sonic Sifter Division, P.O. Box 2405, Milwaukee, Wisconsin 53214, U.S.A.

Bailey Meters and Controls, 218 Purley Way, Croydon, Surrey.
Bausch & Lomb Inc., 820 Linden Avenue, 30320 Rochester, New York 14625, U.S.A.
Bendix Vacuum Ltd, Scientific Instruments and Equipment Division, Easthead Avenue, Wokingham, Berkshire RG11 2PW.
Berg, R., Particle Data Inc., P.O. Box 265, Elmhurst, Illinois 60126, U.S.A.
Brezina, J., Hauptstrasse 68, D-6901 Waldhilsbach, W. Germany.
British Rema, P.O. Box 31, Imperial Steel Works, Sheffield S9 1RA.
Buckbee Mears Co., 245 East 6th Street, St. Paul 1, Minnesota, U.S.A.
Bush, G. F. & Associates, Princeton, New Jersey, U.S.A.

Carl Zeiss, 7082 Oberkochen, W. Germany.
Carl Zeiss Jena Ltd, VEB Carl Zeiss, Jena, W. Germany; also England House, 93-7 New Cavendish Street, London W1.
Carlo Erba, via Carlo Imbonati 24, 20159, Milan, Italy.
Casella, C. F. & Co., Regent House, Britannia Walk, London N1.
Charles Austin Pumps, Petersham Works, 100 Royston Road, Byfleet, Surrey.
Chemisches Laboratorium für Tonindustrie, Goslar, Harz, W. Germany.
Cristison, Albany Road, East Gateshead Industrial Estate, Gateshead, Co. Durham NE8 3AT.
Coleman Instruments Inc., 42 Madison Street, Maywood, Illinois, U.S.A.
Coulter Electronics, High Street, Dunstable, Bedfordshire.
Coulter Electronics, 590 West 20th Street, Hialeah, Florida, U.S.A.

Degenhardt & Co. Ltd, 6 Cavendish Square, London W1.
Delviljem (London) Ltd, Delviljim House, Shakespeare Road, Finchley, Middlesex.
Dietert, H. & Co., 9330 Roselawn Avenue, Detroit, Michigan, U.S.A.
Donaldson Co. Inc., 1400 West 94th Street, Minneapolis, Minnesota 55431, U.S.A.
Draeger Normalair Ltd, Kitty Brewster, Blythe, Northumberland.
Dragerwerk Lubeck, D-24 Lubeck 1, P.O. Box 1339, Moislinger Allee 53-55, W. Germany.

Endecottes Ltd, Lombard Road, London SW19.
Erwin Sick Optik-Elektronik, D-7808 Waldkirch, W. Germany, An der Allee 7-9, Postfach 310.
Evans Electroselenium Ltd, Halstead, Essex.

Ficklen, Joseph, B., 1848 East Mountain Street, Pasadena 7, California, U.S.A.
Fisher Scientific Co., Pittsburgh 19, Pennsylvania, U.S.A.
Fleming Instruments Ltd, Lever Street, Bolton, Lancashire BL3 6BJ.
Foster Instruments, Sydney Road, Muswell Hill, London N10.
Franklin Electronics Inc., Bridgeport, Pennsylvania, U.S.A.
Freeman Labs Inc., 9290 Evenhouse Avenue, Rosemount, Illinois 60018, U.S.A.
Fritsch, Albert & Co., D6580 Idar-Oberstein 1, W. Germany.

Gallenkamp Ltd, Portrack Lane, Stockton-on-Tees, Co. Durham.
Gardner Laboratory, Bethesda, Maryland, U.S.A.

Gelman Hawksley, 12 Peter Road, Lancing, Sussex.
 Gelman Instruments Co., 600 South Wagner Road, Ann Arbor, Michigan 48106, U.S.A.
 General Electric Co., Schenectady, New York, U.S.A.
 Glass Developments Ltd, Sudbourne Road, Brixton Hill, London SW2.
 Glen Creston, The Red House, Broadway, Stanmore, Middlesex.
 Goring Kerr Ltd, Hanover Way, Windsor, Berkshire.
 Greenings, Britannia Works, Printing House Lane, Hayes, Middlesex.
 Griffin & George Ltd, Wembley, Middlesex.

Hawksley & Sons Ltd, 12 Peter Road, Lancing, Sussex.
 High Accuracy Products, Corp., 141 Spring Street, Claremont, California 91711, U.S.A.
 Hird-Brown Ltd, Lever Street, Bolton, Lancashire BL3 6BJ.
 Howe, V. A. & Co. Ltd, 88 Peterborough Road, London SW6.

Image Analysing Computers Ltd, Melbourne, Royston SG6 6ET, Hertfordshire; also 40 Robert Pitt Drive, Monsey, New York 10952, U.S.A.
 Imperial Chemical Industries Ltd, Nobel Division, Stevenston, Ayrshire, Scotland.
 Infrasizers Ltd, Toronto, Ontario, Canada.

Japan Electron Optics Ltd, Jealco House, Grove Park, Edgware Road, Collindale, London NW9; also 477 Riverside Avenue, Medford, Massachusetts 02155, U.S.A.
 Joyce Loeb1 Ltd, Princesway, Team Valley, Gateshead 11, Co. Durham.

Kek Ltd, Hully Road, Hurdsfield Industrial Estate, Macclesfield, Cheshire SK10 2ND.

La Pine Scientific Co., Chicago 29, Illinois, U.S.A.
 Lars, A. B. Ljungberg & Co., Stockholm, Sweden.
 Laser Associates Ltd, Paynes Lane, Rugby, Warwickshire.
 Lavino, Garrard House, 31-45 Gresham Street, London EC2.

Manufacturing Engineering and Equipment Corporation, Warrington, Pennsylvania, U.S.A.
 Mason & Morton Ltd, 32-40 Headstone Drive, Wealdstone, Harrow, Middlesex.
 Metals Research Ltd, 91 King Street, Cambridge.
 Micromeritics Instrum Corporation, 800 Goshen Springs Road, Norcross, Georgia 30071, U.S.A.
 Microscal Ltd, 20 Mattock Lane, Ealing, London.
 Millipore Corp., Ashby Road, Bedford, Massachusetts 01730, U.S.A.
 Mines Safety Appliances Co. Ltd, Greenford, Middlesex.
 Mines Safety Appliances Co. Ltd, 201 Braddock Avenue, Pittsburgh 8, Pennsylvania, U.S.A.
 Mullard Equipment Ltd, Manor Royal, Crawley, Sussex.

Nautamix, N. V., P.O. Box 773, Haarlem, Holland.
 Nethreler & Hinz. GmbH, Hamburg, W. Germany.
 NEU Engineering Ltd, 32-4 Baker Street, Weybridge, Surrey.
 NEU, Etablissement, P.O. Box 28, Lille, France.
 Northgate Traders Ltd, London EC2.

Nuclepore Corp., 7035 Commerce Circle, Pleasanton, California 94566, U.S.A.
 Numek Instruments and Controls Corporation, Appolo, Pennsylvania, U.S.A.
 Numinco, 300 Seco Road, Monroeville, Pennsylvania 15146, U.S.A.

Pascall Ltd, Gatwick Road, Crawley, Sussex.
 Pearson Panke Ltd, 1-3 Halegrove Gardens, London NW7.
 Pennwalt Ltd, Doman Road, Camberley, Surrey.
 Perkin Elmer Ltd, Beaconsfield, Buckinghamshire.
 Phoenix Precision Instrument Co., 3803 Fifth Street, Philadelphia, Pennsylvania 19140, U.S.A.
 Photoelectronics Ltd, Arcail House, Restmor Way, Hockbridge, Wallington, Surrey.
 Pola Laboratory Supplies Inc., New York 7, U.S.A.
 Polaron, 4 Shakespeare Road, Finchley, London N3.
 Polymer Consultants Ltd, London.
 Procdyne Corporation, 221 Somerset Street, New Brunswick, New Jersey, U.S.A.
 Production Sales and Services Ltd, New Malden, Surrey.
 Prosser Scientific Instruments Ltd, Lady Lane Industrial Estate, Hadleigh, Ipswich, Suffolk IP7 6DQ.

Quantachrome Corp., 337 Glen Cove Road, Greenvale, New York 11548, U.S.A.

Rao Instrument Co. Ltd, Brooklyn, New York, U.S.A.

Research Appliance Co., Route 8, Gibsonia, Pennsylvania 15044, U.S.A.

Ronald Trist Controls Ltd, Bath Road, Slough Berkshire.

Rotheroe & Mitchell Ltd, Aintree Road, Greenford, Middlesex.

Royco Instruments, 141 Jefferson Drive, Menlo Park, California 94025, U.S.A.

Sartorius Werke, GmbH, D-34 Gottingen, W. Germany.

Schaar & Co., Chicago, Illinois, U.S.A.

Science Spectrum, 1216 State Street, P.O. Box 3003, Santa Barbara, California, U.S.A.

Sharples Centrifuges, Ltd, Camberley, Surrey.

Shimadzu Seisakusho Ltd, Kanda, Mitoshirocho, Chiyodra-Ku, Tokyo, Japan.

Simon Carves Ltd, Stockport, Lancashire.

Societe Fransaie d'Instruments de Controle et d'Analuses, Le Mesmil, Saint Denise, France.

Sondes Place Research Institute, Dorking, Surrey.

Strohline, Dusseldorf, W. Germany.

Systems and Components Ltd, Broadway, Market Lavington, Devizes, Wiltshire.

Techmation Ltd, 58 Edgware Way, Edgware, Middlesex.

Telefunken, A. E. G., 79 Ulm, Elisabethstrasse 3, W. Germany.

Thermal Control Co. Ltd, 138 Old Shoreham Road, Hove, Sussex.

Thermo-Systems Inc. 2500 Cleveland Avenue, North St. Pauls, Minnesota 55113, U.S.A.

TOA Electric Co., Kobe, Japan.

Ultrasonics Ltd, Otley Road, Bradford, Yorkshire.

V.E.B. Transformatoren und Rontegemwerk, 48 Overbeckstrasse 8030, Dresden, West Germany.

Veco N. V. Zeefplattenfabrick, Eerbeek (Veluwe), The Netherlands.

Vickers Instruments Ltd, Haxby Road, York.

Walther & Co., Aktiengesellschaft, 5 Koln-Dellbruck, W. Germany.

Warmain International Pty Ltd, Artarman, N. S. W., Australia.

Watson, W. & Sons Ltd, Barnet, Hertfordshire.

Zimney Corporation, Monrovia, California, U.S.A.

Part II. Partizle-Size-Related Equipment Noted in Ref. A3.

SAMPLING DEVICES

Spinning Riffler

Sample Divider

Rotary Riffler

Rotary Sample Divider

Sample Splitter

Microscal

Pascal

Freeman Laboratories

Glen Creston

Fritsch (Christison)

FLUE SAMPLERS

Smoke Dust Monitor

BCURA Gas Flow Monitor

Smoke Density meter(chimneys/ducts)

Stack Monitors

In Stack Samplers

Dust Samplers

Smoke Density Measuring Instruments

C.E.R.L. Flue Dust Monitor

High Sensitivity Air Monitor

Airflow Development

Bailey Meters and Controls

Research Appliance Company

Anderson

Anderson

Erwin Sick, Pearson Panke

Foster Instruments

Photoelectronics

AEROSOL SAMPLERS

Thermal Precipitators(Standard
and Long Term)

Gravimetric Dust Sampler

Cascade Impactor, Hexhlet

Casella

(U.S. Agents M.S.A.)

(U.S. Agents M.S.A.)

Wrights T. P.
 Hamiltons T. P.
 Konisampler T. P.
 British Standard Deposit Gauge
 Continuous Oscillating and
 Gravimetric T. P.
 Thermopositor
 Drager Dust Sampler
 Thermal Precipitators, Konimeter,
 Dust
 Collectors, Gravicon, Porticon
 Dust Sampler (filters)
 Electrostatic Air Sampler Kit
 Olin Particle Mass Monitor
 Electrostatic Air Sampler
 Smoke Pollution Sampler
 Cascade Centripeter
 Membrane Filters
 Membrane Filters
 Settlement Dust Counter
 Hexhlet Gravimetric Personal
 Sampler
 Settlement Dust Sampler
 Cascade Impactor
 Portable Dust Sampler
 Periodic Air Sampler
 Personal Sampler
 Cascade Sampler
 Aerosol Gravimetric Spectrometer
 Air Pollution Monitors
 Particle Sampling Unit
 Dust Sampling Unit
 Millipore Sampling Set
 Konimeter
 AERA Portable Air Sampler
 Light Scattering Counters

Light Reflectance Monitor
 Aerosol Spectrometers
 Sigrist Dust Measuring Equip.
 Electricon Smoke Monitor
 Coulter Contamination Counter
 LIDAR, Smoke Plume Tracking
 Laser Light Scattering Particle
 Counter

SIEVING EQUIPMENT

Woven Wire Sieves
 Inclyno Sieve Shaker, Turbine Sifter
 Electroformed Sieves

Electroformed Sieves
 Electroformed Sieves
 Fisher Wheeler Sieve Shaker
 Sieve Shakers
 Sieve Shakers
 Allen-Bradley Sonic Sifter
 Small Portable Sieve Shaker
 Tyler Ro Tap
 Alpine Air Jet
 Wet and Dry Sieve Shakers

Adams
 Adams
 Ficklen
 Glass Developments
 American Instruments

American Instruments
 Dragerwerk
 Sartorius (Howe)

Bendix
 Thermo-Systems, Proner
 Thermo-Systems, Proner
 Charles Austin
 Bird and Tole
 Nuclepore
 Gelman, Millipore
 Casella, M.S.A.
 Casella, M.S.A.

Research Appliances
 Research Appliances
 Rotheroe and Mitchell
 Rotheroe and Mitchell
 Anderson
 Anderson
 Fleming
 Fleming
 Fleming
 Fleming
 Thermal Control
 Carl Zeiss Jena
 Addy Products
 High Accuracy Products (Air Supply)
 Royco (Hawksley)
 Bausch and Lomb (Applied Research
 Laboratories)
 Research Appliance
 Sartorius
 (Howe)
 Ronald Trist
 Coulter
 Laser Associates

Endecottes, Pascall, Greenings
 Pascall
 Buckbee Mears (Production Sales and
 Services)
 Veco
 Endecottes
 Fisher
 American Instruments, Pascall
 Endecottes
 ATM Corporation (Kek)
 La Pine
 La Pine
 Alpine, Lavino
 Fritsch (Howe)

MICROSCOPES

Watson Image Splitting
Push Button Counter
Vicker Image Shearing Eyepiece
Zeiss Endter P.S.A.
Metals Research P.S.A.
Quantimet
MC
Spri Analyser
Superscope Electron Microscope
(also SEMs)
Magnifiers
E.M. Grids
Aides for E.M.
The Timbrell Analyser
The Q.M.S. System

Watson
Casella
Vickers
Carl Zeiss (Degenhardt)
Metals Research
Image Analysing Computers
Millipore
Sondes Place Research

Polaron
Maron and Morton
Alan Agar
Coulter U.S.A.
Bausch and Lomb

MISCELLANEOUS DISPERSING EQUIPMENT

Ultrasonic Dispersers
Pyknometers
Ultrasonic Cleaner
Helium Air Pyknometer
Anti-Static Agent M441
Spraygun for Electron Microscopy

Mullard, Ultrasonics
Numinco
Fritsch (Christison)
Micrometetics (Coulter UK)
I.C.I.
Aerography

SEDIMENTATION EQUIPMENT

Pipettes and Hydrometers
Granulometer
WASP Photosedimentometer
Wagner Turbidimeter
EEL Photosedimentometer
Bound Brook Photosedimentometer
Micromerograph
Shimadzu Sedimentograph

Gallenkamp
Brezina
Microscal
La Pine
Evans
Goring Kerr
Franklin
Shimadzu
Northgate Traders
Sartorius
Bush GF
Pola
Fisher
Schaar
Microscal
Micromeretics (Coulter UK)

Sartorius Sedimentation Balance
Micron Particle Distributometer
Palo-Travis Particle Size Apparatus
Fisher Dotts Apparatus
Travis Method of Two Layer Analysis
LADAL X-Ray Sedimentometer
Sedigraph X-Ray Sedimentometer

CLASSIFIERS

Walther
Cascade Elutriator
Microsplit Separator
Major Classifier
Centrifugal Classifier
Andrews Kinetic Water
Gonell
Haultain Infrasiser
Roller
Bahco
Hexhlet Collector(Walton's Horizontal)
Microplex Classifier
Nauta Hosokawa Classifier
Alanysette 8
Donaldson Classifier

Walther
American Instrument
British Rema
Donaldson
Micromeretics
Griffin and George
Chemisches Laboratorium
Infrasisers
American Instrument
Dietert (Neu)
Casella
Lavino
Nautamix
Fritsch (Howe)
Donaldsons

CENTRIFUGES

Simcar
Joyce Loebel Disc

Simon Carves
Joyce Loebel

Kaye Disc	Martin Sweeny
Sharples Centrifuge	Pennwalt Appliances (U.S.A.)
Whitby Apparatus	Mines Safety
LADAL X-Ray	Microscal
Modified Pipette	Allen
STREAMING PRINCIPLE	
Coulter Counter	Coulter
Celloscope	Lars
P.D. Analyser	Berg
Particle Volume Detector	Telefunken
TOA Microcellcounter	Toa
Granulometer	V.E.B.
LIGHT SCATTERING (see also Aerosol Samplers)	
Shimadzu Light Scattering Photometer	Shimadzu
Sinclair Phoenix Forward	Phoenix
Scattering Light Photometer	Phoenix
Brice-Phoenix L.S.P.	Phoenix
Absolute L.S.P.	American Instruments
Photo-Nephelometers	Coleman
Recording Turbidimeter	General Electric Company
Scattermaster	Manufacturing Engineering Company
Photometers	Shimadzu, Societe Francaise, Nethreler, Polymer Consultants
Differential Light Scattering	Science Spectrum
Photometers	
Atlas of Light Scattering Curve	Science Spectrum
PERMEAMETRY	
Fisher Sub-Sieve Sizer	Kek
Rigden Apparatus	Gallenkamp
Knudsen Flow Permeameter	Micromeretics
The Griffin Surface Area of Powders	Griffin and George
Apparatus	
GAS ADSORPTION (Surface Area and Porosimetry)	
Perkin-Elmer Shell Sorptometer	Perkin-Elmer
Strohline Areameter	Strohlin
Quantasorb and Monosorb	Ameresco, Quantachrome Corporation
Gravimat	Sartorius
A Range of Instruments	Micromeretics (Coulter UK)
Sorptomatic	Carlo Erba (Systems and Components)
Areatron	Leybold
Air Displacement Porometer	Numinco
Surface Area and Gas Adsorption	Numinco
Equipment	
Flow Microcalorimeter	Microscal
Mercury Porosimeters	American Instrument, Carlo Erba (Systems and Components), Micromeretics (Coulter UK), Carlo Erba

A. American National Standards Institute

ANSI B93.28 1973

"Method for Calibration of Liquid Automatic Particle Counters Using AC Fine Test Dust"

ANSI B93.30 1973

"Method of Reporting Contamination Analysis Data of Hydraulic Fluid Power Systems"

ANSI B93.31 1973

"Multi-Pass Method for Evaluating the Filtration Performance of a Fine Hydraulic Fluid Power Filter Element"

ANSI Z168.1

"Analysis by Microscopical Methods for Particle-Size Distribution of Particulate Substances of Sub-Sieve Sizes"

ANSI Z173.31

"Method of Test for Continuous Sizing and Counting of Airborne Particles in Dust-Controlled Areas Based on Light-Scattering Principles"

ANSI Z146.1

"Method for Measuring and Counting Particulate Contamination on Surfaces"

ANSI Z173.5 (1973)

"Method for Sizing and Counting of Airborne Particulate Contamination in Clean Rooms and Other Dust-Controlled Areas Designed for Electronic and Similar Applications"

ANSI 173.16 (1973)

"Method for Sizing and Counting Particulate Contaminants in and on Clean Room Garments"

ANSI B93.19

"Method for Extracting Fluid Samples from the Lines of an Operating Hydraulic Fluid Power System (For Particulate Contamination Analysis)"

ANSI Z173.9

"Method for Identification of Minute Crystalline Particle Contaminants by X-Ray Diffraction"

ANSI PTC28-1973

"Determining the Properties of Fine Particle Matter"

ANSI Z257.3

"Sampling Stalks for Particulate Matter"

B. American Society of Testing and Materials

ASTM E20-68 (1974)

"Analysis by Microscopical Methods for Particle-Size Distribution of Particulate Substances of Sub-Sieve Sizes"

ASTM F321-70T

"Automatic Particle Counter Size Setting"

ASTM F323

"Precision Classification of Particles"

ASTM F490

"Microscopical Sizing and Counting of Particles on Membrane Filters Using Image Shear"

ASTM F312 - 1969

"Microscopic Counting and Sizing of Particles from Aerospace Fluids on Membrane Filters"

ASTM F21.13 Draft in Committee

"Recommended Practice for Particle Count and Size Distribution Measurement in Batch Samples for Filter Evaluation Using an Optical Particle Counter"

ASTM F21.13 Draft in Committee

"Standard Practice for Comparing the Particle-Size Distribution of Solids in a Powder or Suspended in Liquid by Means of Automatic Particle Counters"

ASTM F21.13 Draft in Committee

"Method for the Measurement of Particle Count and Size Distribution in Batch Samples for Filter Evaluation Using an Electrical-Resistance Particle Counter"

ASTM Draft in Committee (F.07.01.05-10)

"Median Method for Particle Counter Single Point Size Calibration"

ASTM Draft in Committee (F.07.01.05-12)

"Practice for Defining Counting and Size Accuracy of a Liquid Borne Particle Counter Using Near-Monodisperse Spherical Particulate Materials"

ASTM Draft in Committee (F.07.01.05-13)

"Recommended Practice for On-Site Calibration of Liquid Borne Automatic Particle Counters with Adjustable Individual Size Thresholds"

ASTM Draft in Committee (F.07.01.05-14)

"Method for Determining the Quality of Calibration Particles for Automatic Particle Counters"

C. National Fluid Power Association

NFPA T2.9.6 1972

"Method for Calibration of Liquid Automatic Particle Counters Using AC Fine Test Dust"

NFPA T3.10.8.8 1973

"Multi-Pass Method for Evaluating the Filtration Performance of a Fine Hydraulic Fluid Power Filter Element"

NFPA T2.9.3 1973

"Method for Reporting the Contamination Analysis Data of Hydraulic Fluid Power Systems"

D. Society of Automotive Engineers

SAE ARP 1192

"Method for Calibration and Verification of Automatic Liquid Borne Counter (Light Method)"

ISO TC 131/SC (USA) N-12

"Method for Calibration of Liquid Automatic Particle Counters Using AC Fine Test Dust"

E. Other ASTM Standards Related to Particle-Size Measurements

1. Material Characterization

Refractory Metals

Fishersizer B330

Turbidimetry B430

Atmospheric Particles

Optical Sizing D2009

Electronic Counter D3365

Alundum Thimble D3563

Pigment-Vehicles D1210

Print Inks D1316

Polymers/Chloride D1705

Soils D422

Whiteware Clays C775

Alumina, Quartz

Air Permeability C721

Electronic Counter C690

Centr. Sedimentation C678

Activated Carbon D2862

White Extender Pigment B3360

Multicolor Lacquers D2338

2. System Characterization

Airborne Collected in Liquid D3365

Airborne Collected in Thimble D3563

Glass-Blow Down Systems

Automatic Counter F327

Manual Measure F308

Aerospace Fluids

Metal/Fiber Ident F314

Microelectronic Components

Ring Oven Technique F59

Non-Cryogenic Fluid Sampling F301

Particles/Matter in Water D1883

Aviation Turbine Fuels D2276

Surfaces F24

Aerospace Fluids/Convoluters F304

Man-Accessible Aerospace Tanks F306

Reservoir-Type Pressure Sensors F305

Aerospace Fluids/Membranes F311

Sampling Stacks D2928

1. Material Characterization (con't)

Soap/Detergents	D502
Metal Ores	E383
Plastics	D1921
Resins	D2451
Asbestos By Screens	D2947
Metal Powders	B293
TFE-Fluorocarbon Matl's.	D1457

During the preparation of this report, a number of bibliographic sources have been used. These include science and engineering indices, books and articles with extensive references, instrument company application notes, and individual journals.

Computer Literature Search

The science abstracts and the engineering index entries for the period 1969 to September 1979 were searched on the key words related to the dimensional measurement of particles, and including instruments, techniques, and calibration methods. Approximately 150 titles and abstracts of papers having varying degrees of relevance were compiled.

Published Sources With Extensive References

Stockham and Fochtman's monograph, Particle Size Analysis (Ann Arbor Science, 1977) contains 58 cited and 42 uncited references on the general subject of its title.

Among the numerous references in the 1976 volume Fine Particles, Willeke and Liu give 50 references related to single particle optical counters and Gebhart and his co-authors give 50 related to optical aerosol size spectrometry above and below the wavelength of light.

Kratohvil's review of the literature on "Light Scattering", which appeared in Analytical Chemistry in 1966, provides 338 references on that subject with explicit consideration given to work on scattering by spherical and nonspherical particles including latexes.

Allen's scholarly chemical-engineering textbook, Particle Size Measurement (Wiley, 1975), contains over 950 references closely related to various aspects of the title subject and also contains names and addresses of international manufacturers and suppliers of particle sampling and size measurement equipment.

Davies' four articles on "Rapid Response Instrumentation" (American Laboratory, Dec. 1973 - Feb. 1974 and April 1978) include over 150 references primarily on equipment commercially available at those times.

McCrone and Delly's encyclopedia of techniques for small particle identification, The Particle Atlas (Edition III, Volume 4, 1973), lists over 2000 references up to 1972 on subjects related to the general subject of particle characterization.

Instrument Company Bibliographies

Coulter Electronics Company provides a listing of over 560 references up to 1975 on the applications of their electrical-resistance type liquid-borne counter such subjects as air contamination and water and sewage.

Pacific Scientific Company provides a listing of nearly 200 references up to 1975 on the application of their HIAC light-obscuration type liquid borne counter on subjects ranging from basic technology to military specifications.

Science Spectrum Company provides a listing of over 70 references up to 1978 on the application of their various light-scattering type instruments on subjects such as microbiology and molecular weights.

Thermo Systems Incorporated provides a listing of 77 references into 1974 on the theory, practice, and applications of instruments such as theirs used for laser doppler velocitometry.

Journals

Articles on the most fundamental aspects of particle size measurement have appeared most frequently in Powder Technology, The Journal of Colloid and Interface Science, Applied

Optics, The Journal of the Optical Society of America, Review of Scientific Instruments,
and The Journal of Microscopy and Microscope.

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U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Calibration

Standard Reference Material 1003

Calibrated Glass Spheres

(5 to 30 Microns)

This standard sample of microscopically measured beads is issued for use in calibrating equipment and in evaluating methods for measuring particle size in the 5 to 30 micron range.

The values given are based on measurements of 10,000 particles, of which 96 percent by volume are spheres. Four particle-size distributions are given with this sample in the form of graphs. These graphs represent a distribution according to volume (figure 1), a distribution according to weight (figure 2), and two Stokes' law distributions (figures 3 and 4). The volume distribution permits comparison with electronic particle counters which respond according to the volume of the particle. The weight distribution permits comparison with ultrafine sieves, and the Stokes' law distributions permit comparison with certain types of sedimentation and elutriation methods.

Four distributions instead of one arise from the fact that some of the beads contain spherical gas voids which are large enough to affect the weight and sedimentation rate of the bead. Void diameters have been measured and corrections applied. The diameters given in the weight and volume distribution (figures 1 and 2) are actual physical diameters. Those given in the Stokes' law distributions (figures 3 and 4) are diameters corresponding to an equivalent distribution of solid spheres, which, on a weight basis, would settle at the same rate as the actual sample. Comparison of figures 3 and 4 shows the effect of a comparatively large change in the density of the sedimentation medium on the calculated Stokes' law distribution of the sample.

The vertical lines in the graph are an estimate of reproducibility based on three times the standard error of the mean for ten samples of 1,000 beads, each of which represents ten subsamples of 100 beads. This corresponds to less than ± 4 percent of the particle diameter for particles smaller than 20 microns with somewhat greater uncertainty for particles larger than this size.

The average specific gravity of the beads for purposes of weight-to-volume conversions is 2.39 ± 0.01 . The specific gravity of the solid glass for Stokes' law calculations is 2.54 based on measurements of a single prism of the same glass. The specific surface computed from microscopic measurements is $1730 \pm 50 \text{ cm}^2/\text{g}$, which corresponds with a specific-surface mean diameter of 14.5 ± 0.4 microns. The sample contains between 500,000 and 600,000 particles per milligram.

Two bottles of beads are provided. It is recommended that each bottle be shaken vigorously for a minute before sampling, and beads be taken from a number of places in each. When the results of the two bottles are analyzed separately, there should be no systematic difference between the two sets of results in excess of the reported reproducibility limits of the sample.

The surface of the glass in these beads can react with atmospheric moisture, which, with time, tends to make them more difficult to disperse. Direct exposure to relative humidities above 90 percent will produce a noticeable effect on dispersibility within three days, whereas the effect is exceedingly slow at relative humidities less than 50 percent, and can be minimized, if not eliminated entirely by storing the beads in a desiccated atmosphere.

Washington, D. C. 20234
July 1, 1965.

W. Wayne Meinke, Chief,
Office of Standard Reference Materials

FIG. 1. VOLUME DISTRIBUTION

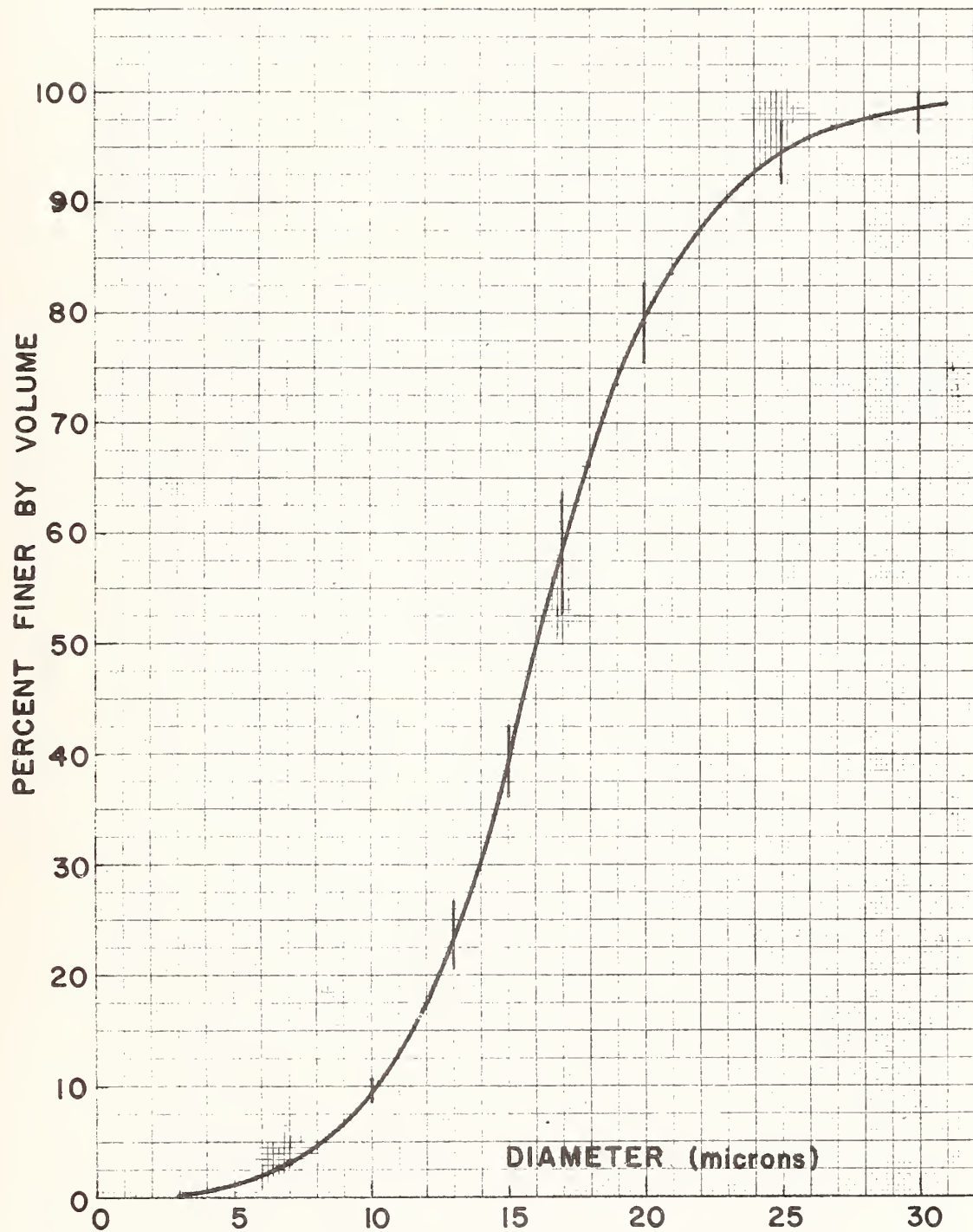


FIG. 2. WEIGHT DISTRIBUTION

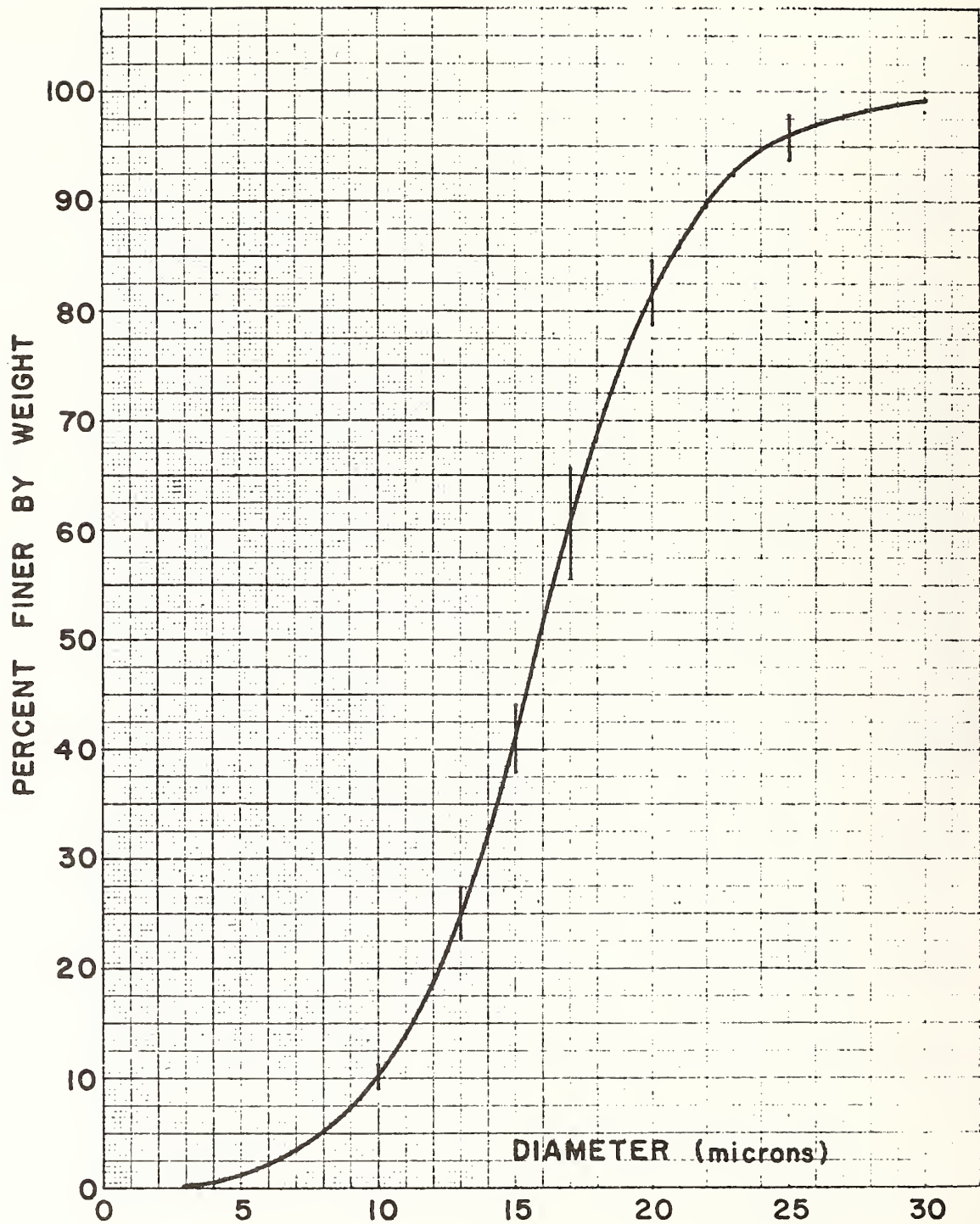


FIG. 3. STOKES' LAW DISTRIBUTION
(CALCULATED FOR WATER)

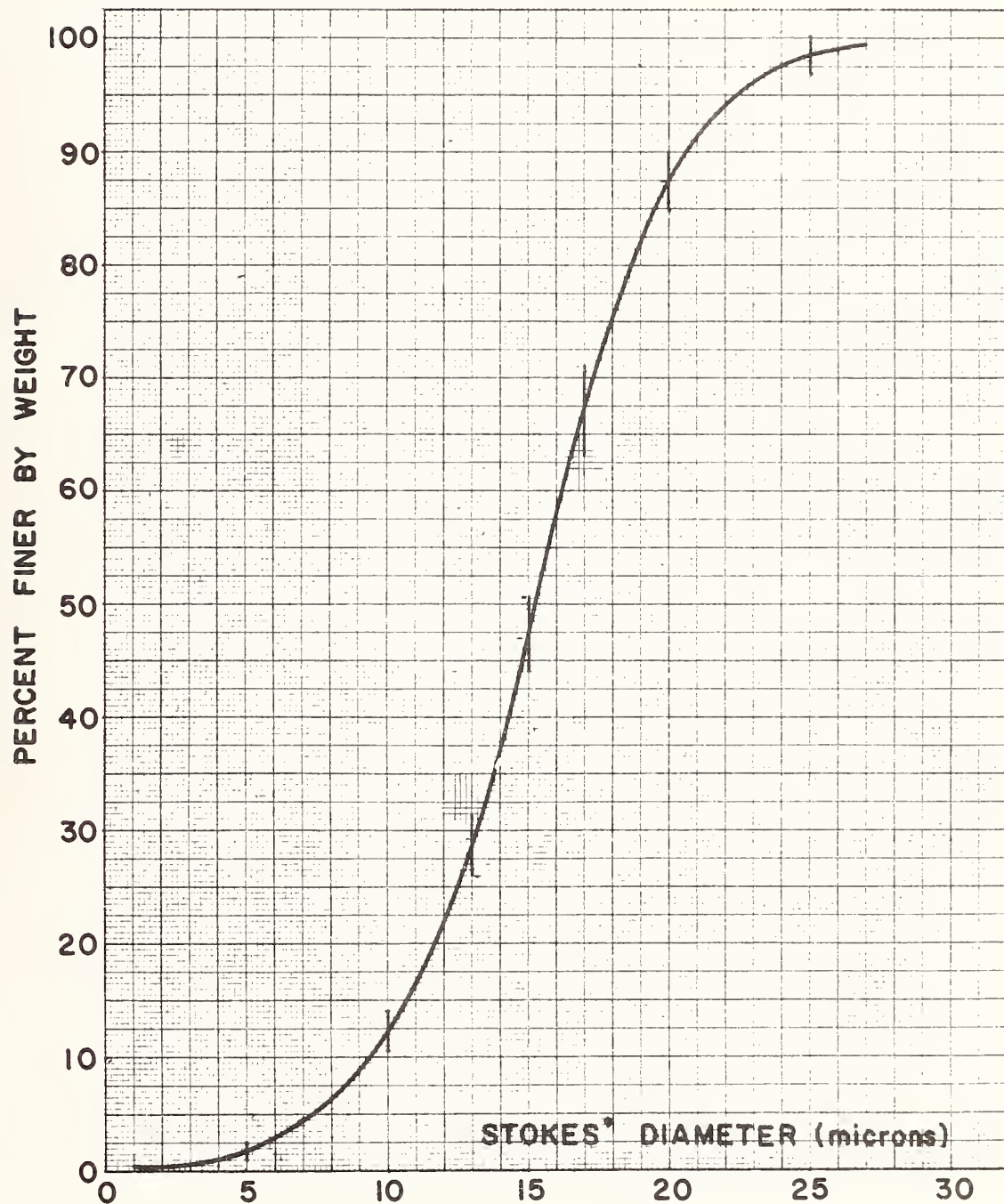
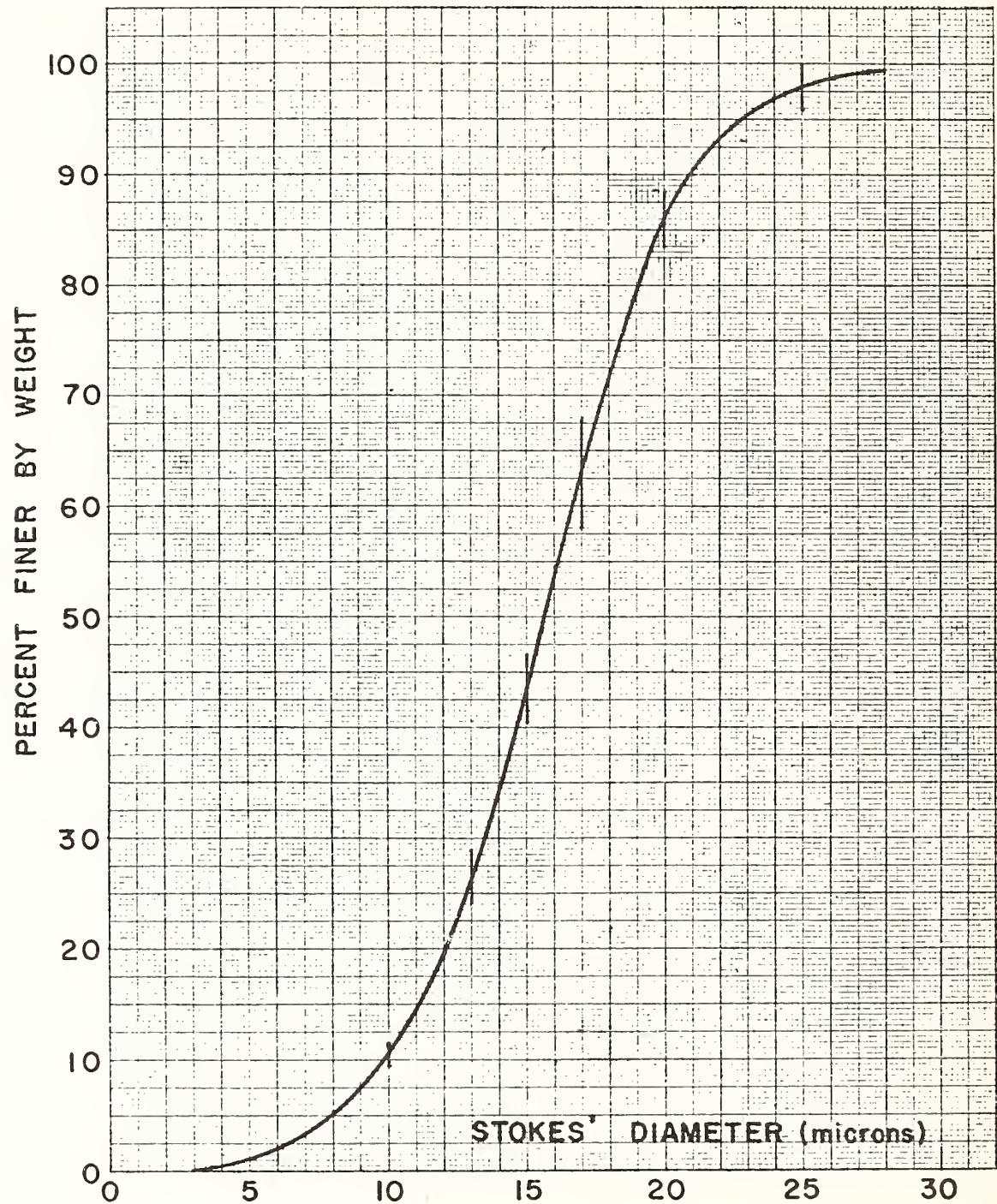


FIG. 4. STOKES' LAW DISTRIBUTION
(CALCULATED FOR AIR)





National Bureau of Standards

Certificate of Calibration

Standard Reference Material 1004

Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-cloth sieves in the range 34 μm through 120 μm (Test Sieve Nos. 400, 325, 270, 230, 200, 170, and 140). The weight of glass beads in each bottle is about 63 g. While most of the beads are spherical about 6 percent by number range from nearly spherical beads to ellipsoidal beads and fused beads.

The distribution of sizes in this SRM as determined by microscopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 13,000 beads were measured in the course of this calibration. These beads were sampled from 6 bottles that were selected at intervals throughout the bottling process. Repeat measurements were made on 2 of the bottles. The beads in these bottles were also carefully compared by sieving with the beads from 21 other bottles, also selected at random. These intercomparisons show no significant difference between beads from all 27 bottles. Considering the values of percent finer to be exact, the mean of the standard deviations associated with each diameter is $0.9 \pm 0.4 \mu\text{m}$. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is calibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 2 \mu\text{m}$, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the care exercised by the operator.

The method that was used in the preparation of these calibrated glass beads (U.S. Patent No. 2,693,706, November 9, 1954) is described in a paper by F. G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Research NBS 47, 139 (1951).

The overall coordination and evaluation of data leading to certification of this SRM was performed by R. K. Kirby.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D. C. 20234
April 3, 1972

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Table 1

Cumulative Size Distribution by Weight

Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)
%	μm	%	μm	%	μm
2	28	34	61	68	89
4	31	36	62	70	90
6	34	38	63		
8	36	40	65	72	92
10	38			74	94
		42	67	76	96
12	40	44	69	78	100
14	42	46	71	80	105
16	45	48	74		
18	47	50	76	82	109
20	49			84	111
		52	78	86	113
22	51	54	80	88	115
24	53	56	82	90	117
26	55	58	83		
28	56	60	84	92	119
30	58			94	121
		62	86	96	123
32	59	64	87	98	126
		66	88		

Directions for Using Calibrated Glass Beads for the
Evaluation of the Effective Opening of Sieves

The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregular shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve cannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G., and Deitz, V. R., *Methods of Sieve Analysis with Particular Reference to Bone Char*, J. Research NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with glass beads, the entire standard is placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed, the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of glazed paper to permit recovery of any beads that may accidentally be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that none of the beads can escape. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a soft brush. Any beads that stick to the funnel should be swept into the weighing bottle with the brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the calibration table.

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 63.30 g. It may be noted that the sum of the weights shows a loss of 0.09 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

Example of calculation for effective opening

U.S. sieve No.	Weight on sieve	Weight percent		Opening of sieve	
		On sieve	Finer than sieve	Effective ^a	Nominal
140	9.99 g	15.81	84.2	111 μm	106 μm
170	5.88	9.30	74.9	95	90
200	14.86	23.50	51.4	77	75
230	8.12	12.84	38.6	64	63
270	6.44	10.19	28.4	56	53
325	7.73	12.23	16.1	45	45
400	3.29	5.21	10.9	39	38
Pan	6.90	10.92			
	63.21				

^aDetermined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a soft brush, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss in weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, a quick check of the accuracy of the beads can be made by "cross-calibrating" a single sieve with the questionable beads and new or relatively little used beads. A variation significantly greater than $\pm 3 \mu\text{m}$ would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Bureau of Standards.

National Bureau of Standards

Certificate of Calibration

Standard Reference Material 1017a

Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-cloth sieves in the range 100 μm through 310 μm (Test Sieves Nos. 140, 120, 100, 80, 70, 60, and 50). The weight of glass beads in each bottle is about 84 g. While most of the beads are spherical about 8 percent by number range from nearly spherical beads to ellipsoidal beads and a few conglomerates.

The distribution of sizes in this SRM as determined by microscopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 60,000 beads were measured in the course of this calibration. These beads were sampled from 24 bottles that were selected at intervals throughout the bottling process. Repeat measurements were made on 7 of the bottles. Considering the values of percent finer to be exact, the mean of the standard deviations associated with each diameter is $4.6 \pm 2.0 \mu\text{m}$. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is calibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 3.5 \mu\text{m}$, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the care exercised by the operator.

The method that was used in the preparation of these calibrated glass beads (U.S. Patent No. 2,693,706, November 9, 1954) is described in a paper by F. G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Research NBS 47, 139 (1951).

The overall coordination and evaluation of data leading to certification of this SRM was performed by R. K. Kirby.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D. C. 20234
September 24, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Table 1

Cumulative Size Distribution by Weight

Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)
%	μm	%	μm	%	μm
1	82	34	163	67	219
2	88	35	165	68	222
3	92			69	226
4	94	36	167	70	229
5	97	37	169		
		38	170	71	232
6	100	39	172	72	235
7	104	40	173	73	238
8	107			74	240
9	110	41	175	75	243
10	112	42	176		
		43	178	76	245
11	114	44	179	77	247
12	116	45	180	78	250
13	118			79	252
14	119	46	181	80	256
15	120	47	182		
		48	184	81	259
16	122	49	185	82	263
17	123	50	186	83	269
18	124			84	274
19	125	51	187	85	279
20	127	52	189		
		53	190	86	283
21	128	54	191	87	287
22	130	55	193	88	291
23	131			89	295
24	133	56	194	90	299
25	135	57	196		
		58	197	91	303
26	137	59	199	92	308
27	140	60	201	93	312
28	143			94	316
29	146	61	203	95	320
30	150	62	205		
		63	207	96	324
31	153	64	210	97	328
32	157	65	213	98	333
33	160			99	341
		66	216		

Directions for Using Calibrated Glass Beads for the Evaluation of the Effective Opening of Sieves

The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregular shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve cannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G., and Deitz, V. R., *Methods of Sieve Analysis with Particular Reference to Bone Char*, J. Research NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with glass beads, the entire standard is placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of paper to permit recovery of any beads that may accidentally be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that no beads can bounce out. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a stiff brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the calibration table.

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 87.46 g. It may be noted that the sum of the weights shows a loss of 0.11 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

Example of calculation for effective opening

U.S. sieve No.	Weight on sieve	Weight percent		Opening of sieve	
		On sieve	Finer than sieve	Effective ^a	Nominal
50	7.81 g	8.94	91.1	304 μm	300 μm
60	11.24	12.87	78.2	250	250
70	9.79	11.21	67.0	219	212
80	19.29	22.09	44.9	180	180
100	12.86	14.72	30.2	150	150
120	8.54	9.77	20.4	127	125
140	11.32	12.96	7.4	105	106
Pan	6.50	7.44			
	87.35				

^a Determined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a sturdy brush, not too stiff, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss in weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, a quick check of the accuracy of the beads can be made by "cross-calibrating" a single sieve with the questionable beads and new or relatively little used beads. A variation significantly greater than $\pm 5 \mu\text{m}$ would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Bureau of Standards.

U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards

Certificate of Calibration

Standard Reference Material 1018a

Calibrated Glass Beads

R. K. Kirby

This Standard Reference Material is intended for use in the evaluation of the effective opening of wire-cloth sieves in the range 225 μm through 780 μm (Test Sieve Nos. 60, 50, 45, 40, 35, 30, and 25). The weight of glass beads in each bottle is about 74 g. While most of the beads are spherical about 6 percent by number range from nearly spherical beads to ellipsoidal beads and fused beads.

The distribution of sizes in this SRM as determined by microscopic measurement is given in Table 1 as the weight percent of glass beads that are smaller than those that have the indicated diameter.

Over 18,000 beads were measured in the course of this calibration. These beads were sampled from 10 bottles that were selected at intervals throughout the bottling process. The beads in these bottles were also carefully compared by sieving with the beads from 20 other bottles, also selected at random. These intercomparisons show no significant difference between beads from all 30 bottles. Considering the values of percent finer to be exact, the standard deviation associated with each test sieve is: No. 60, 2.1 μm ; No. 50, 2.5 μm ; No. 45, 2.9 μm ; No. 40, 2.7 μm ; No. 35, 3.8 μm ; No. 30, 3.3 μm ; and No. 25, 4.5 μm . It was assumed that the effective opening would be within the permissible variation of average opening as specified in the ASTM Standard Specification for Wire-Cloth Sieves, E11-70. This error includes those errors due to the bottling and measuring processes and is to be expected when a given sieve is calibrated with different bottles of this SRM. In addition to this error, the user may impose a sieving error of about $\pm 2 \mu\text{m}$, the result of differing ambient conditions. The reproducibility is, of course, dependent upon the sieving method and the care exercised by the operator.

The method that was used in the preparation of these calibrated glass beads (U. S. Patent No. 2,693,706, November 9, 1954) is described in a paper by F. G. Carpenter and V. R. Deitz, Glass Spheres for the Measurement of the Effective Opening of Testing Sieves, J. Res. NBS 47, 139 (1951).

The overall coordination and evaluation of data leading to certification of this SRM was performed by R. K. Kirby.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D. C. 20234
May 16, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

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Directions for Using Calibrated Glass Beads for the Evaluation of the Effective Opening of Sieves The Calibration Process

The aperture size of a sieve can be determined as the average size of the openings in the sieve. However, the purpose of a sieve is to measure the size of particles, and therefore, it is the effective opening that must be determined. This is done by using particles of known size. Thus the effective opening is determined by the size of calibrated glass beads that will just pass through the sieve. This in turn permits the measurement of the particle size of an unknown material that will also just pass through the sieve.

The openings of a sieve are not all the same size, and particles that are coarser than the average opening can pass through the larger holes. Thus, the effective opening is generally larger than the average opening. In addition, the separation achieved by a sieve is not sharp. A few particles capable of passing the sieve are always retained. The number of particles retained or passed depends upon the manner and time of shaking, and any measurement of the effective opening must take these variables into account. To a large extent, the glass bead method of calibration automatically includes these effects because the sieves are shaken in the same manner when calibrated as when measuring an unknown material.

The sieve openings are essentially square in shape and particles of irregular shape can pass through even though one of the dimensions of the particle is considerably larger than the diameter of the opening. This is especially true for needlelike shapes. The average diameter of such irregular particles that pass a sieve cannot be considered equal to the effective opening of the sieve as measured by the diameter of spheres that just pass.

For the application of the calibrated glass beads to sieve analysis, see Carpenter, F. G. and Deitz, V. R. Methods of Sieve Analysis with Particular Reference to Bone Char, J. Res. NBS 45, 328 (1950).

Calibration Procedure

To evaluate the effective opening of testing sieves with this SRM all of the glass beads are placed on the top sieve. The sieves are then shaken in a shaking device, or by hand, in exactly the same manner as that to be followed in routine analysis.

After the shaking has been completed the stack of sieves is disassembled, and the beads are removed from each sieve and placed into a suitable weighing bottle. Experience has shown that loss of beads is very likely to occur during this operation. Therefore, the whole operation should be carried out over a large piece of paper to permit recovery of any beads that may accidentally be spilled. Such loss can also be minimized by the use of a funnel large enough to completely contain the sieve. The stem of the funnel should be fitted snugly into the mouth of the weighing bottle so that no beads can bounce out. The sieve is inverted into the top of the funnel and all of the glass beads are removed with a stiff brush.

Each of the sieve fractions is weighed to the nearest 0.01 g. After weighing, all beads are returned to the original container and kept for reuse. The weight percent retained on each sieve is calculated from the weights of the sieve fractions. The percent passing through each sieve is determined by subtracting the percentage on the coarsest sieve from 100 percent, the percentage on the next sieve from that result, and so on. The effective size of the sieve opening is determined by interpolation between the nearest values given in the calibration table.

Table 1

Cumulative Size Distribution by Weight

Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (Effective sieve opening)	Weight percent finer	Diameter (effective sieve opening)
%	μm	%	μm	%	μm
1	200	34	349	67	581
2	207	35	354	68	583
3	212			69	585
4	217	36	360	70	588
5	221	37	367		
		38	375	71	590
6	225	39	385	72	592
7	229	40	396	73	595
8	233			74	598
9	236	41	408	75	602
10	239	42	420		
		43	432	76	606
11	242	44	444	77	611
12	245	45	454	78	617
13	249			79	627
14	253	46	462	80	646
15	257	47	469		
		48	475	81	680
16	262	49	480	82	692
17	267	50	486	83	700
18	274			84	706
19	281	51	493	85	712
20	289	52	500		
		53	507	86	717
21	296	54	515	87	723
22	302	55	523	88	729
23	307			89	736
24	312	56	531	90	743
25	316	57	539		
		58	546	91	750
26	320	59	552	92	759
27	323	60	557	93	769
28	326			94	779
29	329	61	561	95	791
30	332	62	565		
		63	569	96	803
31	336	64	572	97	817
32	340	65	575	98	832
33	344			99	849
		66	578		

Example of Calculation Procedure

An example of data and calculations are shown below. Seven sieves were calibrated at the same time. The original weight of the glass beads was 73.91 g. It may be noted that the sum of the weights shows a loss of 0.02 g. This loss is assumed to be evenly distributed and the sum of the weights is used to evaluate the percentages.

Example of calculation for effective opening

U. S. sieve No.	Weight on sieve	Weight percent		Opening of sieve	
		On sieve	Finer than sieve	Effective ^a	Nominal
25	8.43 g	11.41	88.6	733 μm	710 μm
30	7.76	10.50	78.1	618	600
35	18.63	25.21	52.9	506	500
40	7.86	10.64	42.2	422	425
45	4.63	6.27	36.0	360	355
50	10.48	14.18	21.8	301	300
60	5.99	8.11	13.7	252	250
Pan	10.11	13.68			
	73.89				

^aDetermined by interpolation between values given in the calibration table.

Foreign Material and Dirt

If the sieves are not cleaned sufficiently before the calibration, some foreign material will be found among the glass beads. If possible, this foreign material must be removed by hand. A dirty appearance of the glass beads indicates that they have picked up a small amount of dust. The weight of the dust is usually so small that only a negligible error is introduced.

If the sieves to be calibrated have been used they may be cleaned thoroughly with a sturdy brush, not too stiff, soap and water or solvents. Under no circumstance should a sharp object be used to dislodge particles that are stuck in the meshes.

Loss of Weight with Use

Experience has shown that there is a loss of weight of the beads with use. How great a loss can be tolerated without introducing large errors in the calibration is difficult to state. However, the variation of the accuracy of the "working sample" can be monitored by periodically calibrating a set of sieves with it and one or two others that are kept in reserve. A variation significantly greater than $\pm 5 \mu\text{m}$ would indicate that the accuracy of the questionable beads has suffered from a loss of weight. If an SRM is ruined by either repeated use or accident, the only recourse is to purchase a new SRM from the National Bureau of Standards.

National Bureau of Standards

Certificate

Standard Reference Material 484b

Scanning Electron Microscope Magnification Standard (A Stage Micrometer Scale)

David B. Ballard and Fielding Ogburn

This Standard Reference Material is intended for use in calibrating the scanning electron microscope (SEM) magnification scale to an accuracy of 5% or better within the range of 1,000 to 20,000X. Each SRM bears an identification number and has been individually measured.

The certified distances between the centers of specific lines opposite the Knoop indentation (see the sketch on page 2) are provided with each SRM together with a photomicrograph that shows the area used in the measurement. The certification is valid within an area 24 μm wide centered about a line extending from the Knoop indentation.

The distances between the lines were determined from measurements made on photographs taken with an SEM in which each SRM was compared by substitution with a Master Standard; thus each reported interval has been corrected for SEM magnification drift. The operating conditions of the SEM were monitored and a resolution of 0.050 μm was maintained using an SEM resolution test specimen.

The Master Standard was calibrated by an interferometry technique using a helium-neon iodine-stabilized laser as the length standard in the NBS Mechanical Processes Division. The uncertainty of this calibration, based on 160 independent measurements on each spacing, is 0.006 μm for distances from 1 to 50 μm .

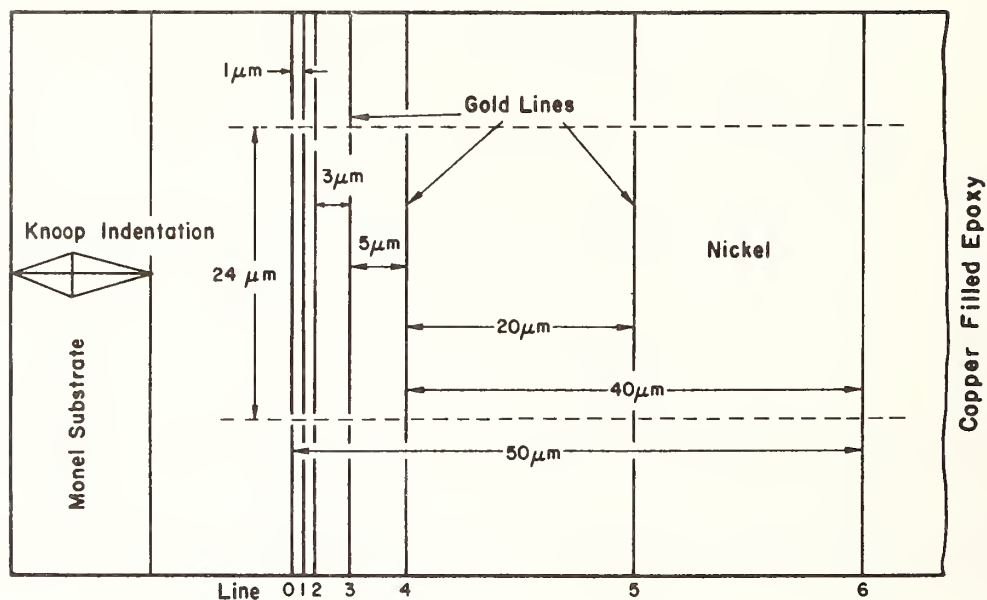
The total uncertainty for the distances between line pairs 0 \rightarrow 1 and 0 \rightarrow 2 (nominal distances of 1 and 2 μm) is 0.032 μm , between line pairs 2 \rightarrow 3 and 3 \rightarrow 4 (nominal distances of 3 and 5 μm) is 0.056 μm , and for the distance between line pair 0 \rightarrow 6 (nominal distance of 50 μm) is 0.580 μm . These total uncertainties are the linear sums of errors associated with the Master Standard calibration and the comparison of each SRM with the Master Standard.

The technical and support aspects involved in the certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.K. Kirby.

Washington, D.C. 20234
November 26, 1980

George A. Uriano, Chief
Office of Standard Reference Materials

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The polished surface of each SRM has been carefully ground and polished using metallographic techniques. The carbonaceous contamination (a product of SEM electron beam bombardment) can be removed by light hand polishing on a stationary surface covered with micro cloth using metallographic 0.05- μm γ -alumina powder. This cleaning process does not alter the certified spacing of the lines by more than 0.010 μm . Other cleaning techniques that remove surface material sufficient to obliterate the Knoop indentation will void the calibrated distance values.

A recommended procedure for calibrating the magnification of the SEM using SRM 484b is given on the following page and by ASTM E766-80 Practice for Calibrating the Magnification of SEM Using SRM 484. It is suggested that the user extend the calibration to adjacent areas outside of the certified area on the SRM for routine use as a "Working Standard." A list of parameters that may affect the resultant magnification of an SEM is given on page 4.

The significant contributions of the following NBS staff members are hereby acknowledged: J.P. Young for techniques of electroplating; D.R. Black for metallographic services; J.S. Beers for calibration of the Master Standard; and M.C. Croarkin for statistical analysis.

The operational steps indicated by the manufacturers of scanning electron microscopes to calibrate the magnification scale are different and often do not consider all the instrument parameters that may change the resultant magnification (see next page). The following procedure details the use of NBS SRM 484b to calibrate one particular SEM, but may be used as a guide for calibration of other SEMs.

Outline of Procedure for Calibrating SEM Magnification Scale

1. After the surface of the SRM 484b has been inspected for cleanliness rigidly mount it on an SEM stub with electrically conductive cement or clamp it onto the SEM stage.
2. The surface of SRM 484b should be normal to the electron beam or the tilt axis of the stage should be perpendicular to the gold lines of the SRM.
3. A clean vacuum of 10^{-2} Pa (10^{-4} Torr) or better is necessary to keep the contamination rate as low as possible.
4. Allow a 30-minute or more warm-up of electronic circuits to achieve operational stability.
5. Adjust electron gun voltage (between 5 to 30 kV), saturate filament, and check filament alignment.
6. Adjust all lens currents at a resettable value. Cycle lens circuit OFF-ON 3 times to minimize hysteresis effects.
7. Adjust lens apertures and stigmator for optimum resolution (minimum astigmatism).
8. SEM resolution should be a minimum of $0.05\text{ }\mu\text{m}$ ($500\text{ }\text{\AA}$), or better.
9. Position the SRM, at a nominal magnification of 1 KX, so that the image of the Knoop indentation is centered at one edge of the viewing cathode ray tube (CRT). The width of the gold line calibrated area extends $12\text{ }\mu\text{m}$ above and below this indentation.
10. The same working distance or magnification scale of the SEM can be reproducibly obtained by focusing on the image of the gold lines with Z axis control at highest possible magnification to minimize depth of focus. An alternate focus method is to use single line wave form ("y" mode) and adjust Z axis for maximum signal height.
11. To minimize the effect of linear distortions produced by the recording system, the procedure is as follows: The SRM is substituted for the unknown sample and photographed. The lines on the SRM to be used in the calibration should be chosen so that the distance between them matches the length of the object to be measured with both images positioned in the same area on the CRT. A millimeter scale taped onto the edges of the CRT in the x and y directions will assist in the relocation of the respective images.
12. Add contrast, if necessary, S/N ratio should be 2:1 minimum.
13. After photo recording, if using Polaroid, allow prints to dry 15 to 20 minutes or more to minimize effects due to emulsion and coating shrinkage.
14. Measure the perpendicular distance between the lines using the *CENTER* of each line image on the photograph with a TEM Diffraction Plate Reader or use an equivalent instrument, the precision of which (about 0.2 mm) is suitable for this purpose.
15. Repeat measurements 3 times on each photograph to determine the average spacing.
16. Magnification =
$$\frac{\text{Distance measured between image lines on photograph}}{\text{Certified distance between same lines}}$$
17. To determine the SEM stability and reproducibility, repeat all steps at hourly or daily intervals or after adjustments and repairs.

PARAMETERS THAT INFLUENCE THE RESULTANT MAGNIFICATION OF AN SEM

The parameters listed below may interact with each other. They are considered in order of their location in the instrument from electron source to the recorded photograph.

1. Electron gun high-voltage instability can change the wavelength of the electrons and thus the final focus.
2. Different condenser-lens strength combinations change the focal point of the final lens.
3. Uncorrected final lens astigmatism can give a false indication of exact focus.
4. Residual magnetic hysteresis, particularly in the final lens, can change the focal conditions.
5. Long depth of focus, particularly at low magnification and small beam divergence controlled by lens and aperture selection, can lead to incorrect focus.
6. Nonorthogonal deflection (x-y axis) can be produced by scan coils.
7. Scan generator circuits may be nonlinear and/or change with aging of circuit components.
8. Zoom control of magnification can be nonlinear.
9. Nonlinearity of scan rotation accessory can distort magnification at different degrees of rotation.
10. Distortion of the electron beam sweep may occur from extraneous magnetic and electrostatic fields.
11. The percent error in magnification may be different for each magnification range.
12. A tilted sample surface (not perpendicular to the beam axis) will introduce foreshortening and magnification variation.
13. The tilt correction applied may not be relative to the tilt axis of the sample or of a particular area on the sample surface.
14. Signal processing, particularly differentiation or homomorphic processing, can give a false impression of focus. DC suppression (sometimes called differential amplification, black level/gain, dark level or contrast expansion) may be used because of the isotropic affect on the image.
15. The objective lens on some instruments may be electrically coupled to the magnification meter, thus focus and magnification are operator dependent.
16. For the same apparent magnification, two different combinations of working distance and beam scan-raster will produce different linear magnification.
17. Thermal and electronic drift of circuit components related to the above parameters can affect magnification with time in a random manner.
18. Distortion of faceplate and nonorthogonal beam deflection of the CRT can produce nonlinear magnification.
19. Camera lens distortion and change of photo image-to-CRT ratio can lead to magnification errors.
20. Expansion or contraction of photographic material, photographic enlarging, and control of contrast, can all have a significant affect on final apparent image magnification.

Tolerances Attached to the
Average Quoted in Certain Tables

The uncertainties attached to the averages are the " $2\sigma_M$ " uncertainties in the mean. The average of N values, assumed to be independent, is given by:

$$\bar{x} = \frac{1}{N} \sum x_1$$

The sample standard deviation σ_S is given by

$$\sigma_S = \left[\frac{1}{N-1} \sum (x_1 - \bar{x})^2 \right]^{1/2}$$

where N is very large.

The " $2\sigma_M$ " uncertainty is given by:

$$2\sigma_M = k_1 \sigma_S$$

where σ_S is the sample deviation, σ_M is the standard deviation or the mean of the population, and k_1 is the factor which relates the sample average deviation and the population standard deviation.

For N small (i.e., less than about 30), the " 2σ limit" differs significantly from the "95% confidence limit". The factor k_2 relates the sample average deviation and the 95% confidence interval:

$$(95\% \text{ confidence interval}) = k_2 \sigma_S.$$

Only as $N \geq 30$, does $K = k_1/k_2$ have a value within about 1% of unity.

The Factors k_1 , K_1 , k_2 , and K_2 are Given in the Following Table
for Various Values of n from 2 to 60

Number of Determinations	Unbiased Estimator	$2\sigma_m$ Estimator	Sample 95% Confidence	Mean 95% Confidence	
n	$k_1[1]$	k_1	$k_2[2]$	k_2	$\frac{k_1}{k_2}$
2	0.797	1.77	12.71	8.99	0.20
3	0.886	1.30	4.30	2.48	0.52
4	0.921	1.09	3.18	1.59	0.69
5	0.940	0.95	2.78	1.24	0.77
6	0.952	0.86	2.57	1.05	0.82
7	0.959	0.79	2.45	0.93	0.85
8	0.965	0.73	2.37	0.84	0.87
20	0.987	0.45	2.09	0.47	0.94
30	0.991	0.37	2.04	0.37	1.00
60	0.996	0.26	2.00	0.26	1.00

1. Natrella, M. G. and C. Eisenhart, "Basic Statistical Concepts and Preliminary Considerations," NBS Handbook 91 (1966).*
2. Ku, H., "Statistical Concepts in Metrology," Handbook of Industrial Metrology, ASTM, Prentice Hall (1967).*

* Reprinted in Precision Measurement and Calibration: Statistical Concepts and Procedures, NBS SP-300, Vol. I (Feb. 1969).

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11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> This report surveys generic techniques for the dimensional calibration of microscopic particle size standards. It notes some user needs and available instrumentation, documentary standards, and commercial, sized particles. It discusses the elements of the measurement process, including the particle and medium, size-dependent phenomena, shape factors, single-number indices of average size, and means of length calibration. The report examines systematic differences among published results of electron microscopy, light scattering, particle counter, and other measurements on widely-used commercial polymer spheres. It concludes that the definitive calibration of narrow-distribution polymer spheres, a prerequisite first step toward calibration of irregularly-shaped matter, would best involve a three-element approach involving the techniques named.			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> dimensional measurement; electron microscopy; flow-through particle counters; latex spheres; light scatter; micrometrology; microscopic spheres; Mie scattering; optical microscopy; particle standards; particle size calibration; polymer spheres; scanning electron microscope; transmission electron microscope. Availability <input checked="" type="checkbox"/> Unlimited <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input checked="" type="checkbox"/> Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. <input type="checkbox"/> Order From National Technical Information Service (NTIS), Springfield, VA. 22161			14. NO. OF PRINTED PAGES 150 15. Price \$5.50

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